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SEPARATION OF ANGLES IN THE TWO-ELECTRON PROBLEM

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(Received February 3, 1930)

Abstract

Neglecting the spin, two electrons are described in quantum mechanics by means of a wave equation in six variables. It is shown that well-known relations between angular momentum operators make it possible to determine the dependence of the wave function on three variables. The problem is thus reduced from *six* to *three* dimensions. For a state with an assigned "orbital" angular momentum l, say an S, P, D state the dependence of the wave function on three Euler angles is determined by the value of l. The wave function is a linear combination of products of distance and angle functions, the latter depending only on the three Euler angles. The angle functions are well-known solutions of the wave equation for a symmetrical top. The distance functions satisfy wave equations in three variables r_1, r_2, r_{12} or r_1, r_2, θ. The case of P terms is worked out in detail. Equations (10), (25) apply to two electrons having the *same azimuthal quantum number*. Equations (18), (20), (24) describe all the other cases, for instance S and P electrons combining to give ^1P and ^3P. Triplets are described by (18) and singlets by (20).

TWO electrons are treated in quantum mechanics by means of a six dimensional wave equation. In most atomic problems it is sufficient to consider the two electrons under the influence of a central field of force and to treat all other questions by perturbation methods. It is well known that in this approximation essential simplifications are introduced by the spherical symmetry of the central field of force. The eigenfunctions may be arranged in non-combining systems, each system corresponding to a certain value of the total angular momentum. By considerations of this sort it has been shown that correct space quantization, multiplet intensity relations, selection rules, and anomalous Zeeman effect formulas are consequences of quantum mechanics.†

In the calculations of the two or many electron problem it is customary at present to employ an approximation method such as Hartree's and to

† See in particular E. Wigner, Zeits. f. Physik **43**, 624 (1927) and especially p. 640 where the general possibility of (6) below is pointed out. The difference between the present treatment and Wigner's lies in the use of (4) with its known system of eigenfunctions.

consider each electron as subject to the action of a central field of force. In the calculations of the normal energy levels of He, however, Hylleraas[1] found it useful to consider the problem exactly. His calculations apply to the S states, which reduces the problem to a three dimensional one. We shall see that the reduction from six to three dimensions can be always made and that it is an immediate consequence of the spherical symmetry of the field. Even though the solution of a three dimensional wave equation is difficult we believe to have simplified the general problem because the application of variational methods, such as the Ritz method to a six or five dimensional problem is usually out of the question.

Let ψ be the Schroedinger function. Let the coordinates of the electrons be (x_1, y_1, z_1), (x_2, y_2, z_2). By the general theorem of conservation of angular momentum

$$\left[\sum_{x,y,z}\left(y_1\frac{\partial}{\partial z_1}-z_1\frac{\partial}{\partial y_1}+y_2\frac{\partial}{\partial z_2}-z_2\frac{\partial}{\partial y_2}\right)^2+l(l+1)\right]\psi=0 \tag{1}$$

for any state with angular momentum l. Introducing polar coordinates (r_1, θ_1, ϕ_1), (r_2, θ_2, ϕ_2) this becomes

$$\begin{aligned}\Big\{&\Big(\sin\phi_1\frac{\partial}{\partial\theta_1}+\cos\phi_1\frac{\cos\theta_1}{\sin\theta_1}\frac{\partial}{\partial\phi_1}+\sin\phi_2\frac{\partial}{\partial\theta_2}+\cos\phi_2\cot\theta_2\frac{\partial}{\partial\phi_2}\Big)^2\\&+\Big(-\cos\phi_1\frac{\partial}{\partial\theta_1}+\sin\phi_1\cot\theta_1\frac{\partial}{\partial\phi_1}-\cos\phi_2\frac{\partial}{\partial\theta_2}+\sin\phi_2\cot\theta_2\frac{\partial}{\partial\phi_2}\Big)^2\\&+\Big(\frac{\partial}{\partial\phi_1}+\frac{\partial}{\partial\phi_2}\Big)^2+l(l+1)\Big\}\psi=0.\end{aligned} \tag{2}$$

We now reexpress ψ in terms of Euler angles θ', ϕ',ϕ and r_1, r_2, θ connected by the transformation formulas:

$$\theta'=\theta_1,\quad \phi'=\phi_1$$

$$\begin{aligned}&\cos\theta=\cos\theta'\cos\theta_2+\sin\theta'\sin\theta_2\cos(\phi_2-\phi_1); && \sin\theta_2\sin\alpha=\sin\theta'\sin\phi\\&\cos\theta_2=\cos\theta'\cos\theta-\sin\theta'\sin\theta\cos\phi; && \sin\theta\sin\alpha=\sin\theta'\sin(\phi_2-\phi_1)\\&\cos\theta'=\cos\theta_2\cos\theta+\sin\theta_2\sin\theta\cos\alpha; && \sin\theta\sin\phi=\sin\theta_2\sin(\phi_2-\phi_1)\end{aligned} \tag{3}$$

the notation being throughout as in the first paper of Hylleraas. The angle θ drops out of (2) which reduces itself to

$$\left\{\frac{\partial^2}{\partial\theta'^2}+\cot\theta'\frac{\partial}{\partial\theta'}+\frac{1}{\sin^2\theta'}\frac{\partial^2}{\partial\phi^2}-2\frac{\cos\theta'}{\sin^2\theta'}\frac{\partial^2}{\partial\phi\partial\phi'}+\frac{1}{\sin^2\theta'}\frac{\partial^2}{\partial\phi'^2}+l(l+1)\right\}\psi=0. \tag{4}$$

[1] Hylleraas, Zeits. f. Physik **54**, 347 (1929); **48**, 469 (1928). See also J. C. Slater, Proc. Nat. Acad. **13**, 423 (1927); G. W. Kellner, Zeits. f. Physik **44**, 91 (1927).

[2] For derivation see appendix I.

This is a well-known equation, being a special case of the wave equation for a symmetrical top. Its eigenwerte are known to correspond to integral values of l, the value zero being included. The angular momentum about the z axis is represented by the operator

$$Mz=\frac{h}{2\pi i}\left(x_1\frac{\partial}{\partial y_1}-y_1\frac{\partial}{\partial x_1}+x_2\frac{\partial}{\partial y_2}-y_2\frac{\partial}{\partial x_2}\right)=\frac{h}{2\pi i}\left(\frac{\partial}{\partial\phi_1}+\frac{\partial}{\partial\phi_2}\right)=\frac{h}{2\pi i}\frac{\partial}{\partial\phi'}. \tag{5}$$

If $l(l+1)=0$ there are no eingfunctions (4) except those which do not depend on θ', ϕ, ϕ'. Thus for $l=0$ the wave function depends only on r_1, r_2, θ or r_1, r_1, r_{12} as pointed out by Hylleraas for S states. In all other cases i.e. for P, D, states ψ depends on the angles. Thus for P states ($l=1$) we have the following nine independent eigenfunctions

$$\cos\theta',\ (1+\cos\theta')e^{\pm i(\phi+\phi')},\ e^{\pm i\phi}\sin\theta',\ e^{\pm i\phi'}\sin\theta',\ (1-\cos\theta')e^{\pm i(\phi-\phi')}.$$

We may say therefore that for any P state

$$\psi=\sum_{i=1}^{9} f_i(r_1,r_2,\theta)u_i(\theta',\phi',\phi) \tag{6}$$

where $u_1,\ \cdots\ u_9$ are the above set of nine independent eigenfunctions. Equation (6) is, however, too general because the nine eigenfunctions can be subdivided into three non-combining sets, each set containing three functions, all the functions of a given set depending on ϕ' as $e^{im\phi'}$. According to (5) each set describes such an orientation of the total angular momentum that its component along OZ is $mh/2\pi$. For $m=0$ such a set of functions is

$$\cos\theta',\ e^{\pm i\phi}\sin\theta'. \tag{6'}$$

In (6) therefore, it is permissible to extend the summation only over these three functions if we are interested only in solutions with $m=0$. The legitimacy of using only these three functions is of course a consequence of the invariance of the Hamiltonian under rotations about the z axis. On account of this invariance the result of operating by the Hamiltonian on any term in (6) gives rise to angular functions with the same value of m. In the general expression (6) therefore each set of functions is entirely independent of the other two.

Since the two electrons are equal we have a further subdivision into non-combining term systems. This is the usual subdivision into symmetric and antisymmetric solutions. With this in mind we use Hylleraas' expressions (23), (24) according to which the Schroedinger equation for the energy is

$$\frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial\psi}{\partial r_1}\right)+\frac{1}{r_2^2}\frac{\partial}{\partial r_2}\left(r_2^2\frac{\partial\psi}{\partial r_2}\right)+\frac{1}{r_1^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+A_1[\psi]\right]$$

$$+\frac{1}{r_2^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+A_2[\psi]\right]+8\pi^2mh^{-2}(E-V)\psi=0$$

$$A_1[\psi]=(\cot^2\theta+2\cot\theta\cot\theta'\cos\phi+\cot^2\theta')\frac{\partial^2\psi}{\partial\phi^2}+\frac{1}{\sin\theta'}\frac{\partial}{\partial\theta'}\left(\sin\theta'\frac{\partial\psi}{\partial\theta'}\right)$$
$$+\frac{1}{\sin^2\theta'}\frac{\partial^2\psi}{\partial\phi'^2}+2\cot\theta'\sin\phi\frac{\partial^2\psi}{\partial\theta\partial\phi}-2\cos\phi\frac{\partial^2\psi}{\partial\theta\partial\theta'}-2\frac{\sin\phi}{\sin\theta'}\frac{\partial^2\psi}{\partial\theta\partial\phi'}$$
$$+2\cot\theta\sin\phi\frac{\partial^2\psi}{\partial\phi\partial\theta'}-\frac{2}{\sin\theta'}(\cot\theta'+\cot\theta\cos\phi)\frac{\partial^2\psi}{\partial\phi\partial\phi'};\quad A_2[\psi]=\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\tag{7}$$

On account of spherical symmetry V is a function of r_1, r_2, θ only and does not contain θ', ϕ', ϕ. The functions u_i behave therefore as constant coefficients with the exceptions of the terms $A_1[\psi]$, $A_2[\psi]$. Since by (3) $\sin\theta'\sin\phi=\sin\theta_2\sin\alpha$, the angular eigenfunction $\sin\theta'\sin\phi$ is seen to be antisymmetric in the electrons 1 and 2. For this reason A_1 and A_2 must produce similar effects on it. In fact it is found that

$$A_1[\sin\theta'\sin\phi]=A_2[\sin\theta'\sin\phi]=-\sin^{-2}\theta(\sin\theta'\sin\phi).\tag{8}$$

We see therefore that the particular linear combination of two of the eigenfunctions for $m=0$, namely $\sin\theta'\cdot\sin\phi$ when operated on by the Hamiltonian gives rise to itself only. A possible P state is therefore given by

$$\psi=f(r_1,r_2,\theta)\sin\theta'\sin\phi\tag{9}$$

and the differential equation for f is

$$\frac{\partial}{r_1^2\partial r_1}\left(r_1^2\frac{\partial f}{\partial r_1}\right)+\frac{\partial}{r_2^2\partial r_2}\left(r_2^2\frac{\partial f}{\partial r_2}\right)+(r_1^{-2}+r_2^{-2})\left[\frac{\partial}{\sin\theta\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)-\frac{f}{\sin^2\theta}\right]$$
$$+8\pi^2mh^{-2}(E-V)f=0.\tag{10}$$

This differential equation differs from the one for S states only by the term $-(r_1^{-2}+r_2^{-2})\sin^{-2}\theta$ and it is seen that the determination of its eigenvalues can be carried out by analogous methods. The physical interpretation of the solutions (9) becomes apparent if the perturbation e^2/r_{12} between the two electrons is supposed small. Then (10) is separable. Supposing the separation to take place by

$$f=P_n^{(1)}(\cos\theta)g(r_1,r_2)\tag{10'}$$

we obtain

$$\frac{\partial}{r_1^2\partial r_1}\left(r_1^2\frac{\partial f}{\partial r_1}\right)+\frac{\partial}{r_2^2\partial r_2}\left(r_2^2\frac{\partial f}{\partial r_2}\right)-n(n+1)(r_1^{-2}+r_2^{-2})f+8\pi^2mh^{-2}(E-V)f=0.$$

This may be considered as the radial part of the Schroedinger equation for two electrons, each being initially in a state with azimuthal quantum number n. The same may be seen from (10') because by (3)

$$\sin\theta\sin\theta'\sin\phi=\sin\theta_1\sin\theta_2\sin(\phi_2-\phi_1)$$

so that the angular part of (10′) is a linear combination of products of the type $P_n^1(\cos\theta_1)\, e^{\pm i\phi_1}$. The solution (9) represents therefore P states which arise either from two ^2P or two ^2D or two ^2F electrons etc. The solutions of (10) may be symmetric or antisymmetric in r_1, r_2 giving the singlet and triplet systems. They include the case of equivalent orbits.

Out of the three functions (6′) we have left now only two

$$\cos\theta',\ \sin\theta'\cos\phi$$

substituting these into (7) it is found that the Hamiltonian operating on one of them gives rise not only to itself but also to the other. Here we must write

$$\psi = f_1\cos\theta' + f_2\sin\theta'\cos\phi. \tag{11}$$

Operating on this by (7) we get two simultaneous linear equations in f_1 and f_2:

$$\begin{aligned} L[f_1] - 2r_1^{-2}\left(f_1 + \cot\theta f_2 + \frac{\partial f_2}{\partial\theta}\right) &= 0 \\ L[f_2] + r_1^{-2}\left(2\frac{\partial f_1}{\partial\theta} - \sin^{-2}\theta f_2\right) - r_2^{-2}\sin^{-2}\theta f_2 &= 0 \end{aligned} \tag{12}$$

where

$$\begin{aligned} L[f] = \frac{\partial}{r_1^2\partial r_1}\left(r_1^2\frac{\partial f}{\partial r_1}\right) + \frac{\partial}{r_2^2\partial r_2}\left(r_2^2\frac{\partial f}{\partial r_2}\right) \\ + (r_1^{-2}+r_2^{-2})\frac{\partial}{\sin\theta\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) + 8\pi^2 m h^{-2}(E-V)f. \end{aligned} \tag{13}$$

Equations (11), (12) are unsymmetrical in (1) and (2). Making the substitutions

$$F_1 = f_1 + \cot\theta\cdot f_2,\quad F_2 = (\sin\theta)^{-1} f_2 \tag{14}$$

we have

$$\psi = F_1\cos\theta_1 - F_2\cos\theta_2 \tag{15}$$

while (12) goes into[3]

$$\begin{aligned} L[F_1] + \frac{2}{r_1^2}\left(\cot\theta\frac{\partial F_1}{\partial\theta} - F_1\right) + \frac{2\partial F_2}{r_2^2\sin\theta\partial\theta} &= 0 \\ L[F_2] + \frac{2\partial F_1}{r_1^2\sin\theta\partial\theta} + \frac{2}{r_2^2}\left(\cot\theta\frac{\partial F_2}{\partial\theta} - F_2\right) &= 0. \end{aligned} \tag{16}$$

Here F_1, F_2 are functions of r_1, r_2, θ only. Any ψ in (15) must be either symmetric or antisymmetric in (1) and (2). The latter case is obtained if

$$F_2(r_1, r_2, \theta) = F_1(r_2, r_1, \theta) \equiv \bar{F}(r_1, r_2, \theta). \tag{17}$$

[3] For direct derivation see Appendix II.

Letting $F=F_1$ the two equations (16) reduce to a single equation in F *vis.*

$$L[F]+\frac{2}{r_1^2}\left(\cot\theta\frac{\partial F}{\partial\theta}-F\right)+\frac{2}{r_2^2\sin\theta}\frac{\partial\tilde{F}}{\partial\theta}=0. \tag{18}$$

The symmetric solutions are obtained by letting

$$F_2=-\tilde{F}_1. \tag{19}$$

Here we write $F_1=G$ and (16) reduces again to a single equation

$$L[G]+\frac{2}{r_1^2}\left(\cot\theta\frac{\partial G}{\partial\theta}-G\right)-\frac{2}{r_2^2\sin\theta}\frac{\partial\tilde{G}}{\partial\theta}=0. \tag{20}$$

The only difference between (18) and (20) is in the sign of the last term. This term represents the resonance between the two electrons. In the unperturbed state i.e. if the perturbation term e^2/r_{12} is not important the simplest solutions of (18) are those for which $(\partial F/\partial\theta)=0$. Then (15) shows that we deal with a ^3P term arising from a ^2S and a ^2P electron while similarly the solutions of (20) give the corresponding ^1P terms. In addition to these solutions there are others for the unperturbed case. Thus if we set

$$F=g(r_1,r_2)\cos\theta+\tilde{g}/3$$

we find from (15) that

$$\psi=g(\cos\theta\cos\theta_1-\cos\theta_2/3)-\tilde{g}(\cos\theta\cos\theta_2-\cos\theta_1/3).$$

Since

$$\cos\theta\cos\theta_1-\cos\theta_2/3=\tfrac{2}{3}\cos\theta_2P_2(\cos\theta_1)-\cos\theta_1\sin\theta_1\sin\theta_2\cos(\phi_2-\phi_1)$$

this angular function is seen to consist of a linear combination of

$$e^{\pm im\phi_1}P_2{}^m(\cos\theta_1)\quad\text{and}\quad e^{\pm im\phi_2}P_1{}^m(\cos\theta_2).$$

This is a case of ^2P and ^2D terms combining to give a ^3P. In a similar way all other combinations between electrons of unequal azimuthal quantum number resulting in P terms are contained among the solutions of (18).

Summarizing the classifications of all solutions belonging to the subset (6′) we may say that (9) and (10) give the P terms arising from electrons which in the unperturbed state have equal azimuthal quantum numbers while (15), (18), (20) give the P terms arising from all other electron combinations.

It will be remembered now that equation (6) contains two more non-combining sets of eigenfunctions corresponding to $m=\pm1$. The spherical symmetry of the problem enables us to write them down by analogy with those already found. Thus corresponding to (15) and (18) we have now a complete set of orthogonal eigenfunctions

$$
\begin{aligned}
u_1 &= (3^{1/2}/4\pi)(F\sin\theta_1 e^{i\phi_1} - \tilde{F}\sin\theta_2 e^{i\phi_2}) \\
&= (3^{1/2}/4\pi)[a\sin\theta' + b(-i\sin\phi - \cos\theta'\cos\phi)]e^{i\phi'} \\
u_0 &= (6^{1/2}/4\pi)(F\cos\theta_1 - \tilde{F}\cos\theta_2) = (6^{1/2}/4\pi)[a\cos\theta' + b\sin\theta'\cos\phi] \qquad (21) \\
u_{-1} &= (3^{1/2}/4\pi)(F\sin\theta_1 e^{-i\phi_1} - \tilde{F}\sin\theta_2 e^{-i\phi_2}) \\
&= (3^{1/2}/4\pi)[a\sin\theta' + b(i\sin\phi - \cos\theta'\cos\phi)]e^{-i\phi'} \\
a &= F - \tilde{F}\cos\theta, \quad b = \tilde{F}\sin\theta.
\end{aligned}
$$

The normalization being such that

$$
\int (F^2 - 2F\tilde{F}\cos\theta + \tilde{F}^2)dV_{r_1,r_2,\theta} = 1; \quad dV_{r_1,r_2,\theta} = r_1^2 r_2^2 \sin\theta dr_1 dr_2 d\theta .
$$

These three eigenfunctions belong to the eigenwerte of (18) and are to be used together in solving perturbation problems such as fine structure calculations. Similarly there are three other eigenfunctions for every solution of (20). The remaining three functions are of the type (9). We note that $\sin\theta\sin\phi = R_z/R$ where $R_z = [\vec{r}_1 \times \vec{r}_2]$. Forming the combinations $R_x \pm iR_y$ we find this set of functions to be

$$
\begin{aligned}
&[(3^{1/2}/4\pi)e^{i\phi'}(i\cos\phi - \cos\theta'\sin\phi), \quad (6^{1/2}/4\pi)\sin\theta'\sin\phi, \\
&\qquad (3^{1/2}/4\pi)e^{-i\phi'}(-i\cos\phi - \cos\theta'\sin\phi)]f.
\end{aligned} \qquad (22)
$$

The differential equations (16), (18) and the corresponding sets of eigenfunctions (21), (22) correspond to essentially different cases and for this reason the variational equations belonging to the two cases are different. We consider the type of solution described by (16) and (21) first. The variational equation belonging to the problem is

$$
\delta \int \left\{ \left(\frac{\partial\psi}{\partial x_1}\right)^2 + \cdots + \left(\frac{\partial\psi}{\partial z_2}\right)^2 + 8\pi^2 m h^{-2}(V - E)\psi^2 \right\} dx_1 \cdots dz_2 = 0 \qquad (23)
$$

with the equation of condition

$$
\int \psi^2 dx_1 \cdots dz_2 = 1. \qquad (23')
$$

Here $dx_1 \cdots dz_2$ is the volume element of the six dimensional configuration space. Taking any of the functions (21) the volume element may be reexpressed in terms of r_1, r_2, θ, θ', ϕ', ϕ and the integrations may then be performed over the angles θ', ϕ', ϕ in (23) and (23′).

The result of the calculation is:[4]

$$
\begin{aligned}
\delta \int \Bigg\{ &\left(\frac{\partial F_1}{\partial r_1}\right)^2 - 2\cos\theta \frac{\partial F_1}{\partial r_1}\frac{\partial F_2}{\partial r_1} + \left(\frac{\partial F_2}{\partial r_1}\right)^2 + \left(\frac{\partial F_1}{\partial r_2}\right)^2 - 2\cos\theta \frac{\partial F_1}{\partial r_2}\frac{\partial F_2}{\partial r_2} + \left(\frac{\partial F_2}{\partial r_2}\right)^2 \\
&+ (r_1^{-2} + r_2^{-2})\left[\left(\frac{\partial F_1}{\partial\theta}\right)^2 - 2\cos\theta \frac{\partial F_1}{\partial\theta}\frac{\partial F_2}{\partial\theta} + \left(\frac{\partial F_2}{\partial\theta}\right)^2\right] + 2r_1^{-2}F_1^2 + 2r_2^{-2}F_2^2
\end{aligned}
$$

[4] For derivation see appendix II.

$$+2r_1^{-2}\sin\theta F_1\frac{\partial F_2}{\partial\theta}+2r_2^{-2}\sin\theta F_2\frac{\partial F_1}{\partial\theta}$$
$$+8\pi^2mh^{-2}(V-E)(F_1^2-2F_1F_2\cos\theta+F^2{}_2)\Big\}dV_{r_1r_2\theta}=0 \tag{24}$$

and the equation of condition is

$$\int(F_1^2-2F_1F_2\cos\theta+F_2^2)dV_{r_1,r_2,\theta}=1. \tag{24'}$$

Performing independent variations of F_1 and F_2 the differential equations (16) follow from (24). Corresponding to (17) and (18) the variational equation (24) gives two different equations, one applying to an antisymmetric ψ and the other to the symmetric one. Each of these involves only one function and its transposed and can be worked out by the same method as used by Hylleraas. It will be noted that the antisymmetric solutions (24) involve combinations of the type $F^2-2F\tilde{F}\cos\theta+\tilde{F}^2$. If $r_1=r_2$, this vanishes for $\theta=0$, so that the values of $F(r, r, \theta)$ are not important. On the other hand for the symmetric solutions $G(r, r, \pi)$ are not important. It will be noted also that both the differential equation and the variational one involve simultaneously a function of r_1, r_2, θ and its transposed and that *the dependence on θ is of primary importance in determining the difference between symmetric and antisymmetric solutions.*

The variational equation corresponding to (10) can be written down by inspection and is

$$\delta\int\Big\{\Big(\frac{\partial f}{\partial r_1}\Big)^2+\Big(\frac{\partial f}{\partial r_2}\Big)^2+(r_1^{-2}+r_2^{-2})\Big[\Big(\frac{\partial f}{\partial\theta}\Big)^2+\frac{f^2}{\sin^2\theta}\Big]$$
$$+8\pi^2mh^{-2}(V-E)f^2\Big\}dV_{r_1,r_2,\theta}=0 \tag{25}$$

with the equation of condition

$$\int f^2dV_{r_1,r_2,\theta}=1. \tag{25'}$$

This differs from the equation used by Kellner and Hylleraas only by the term $(r_1^{-2}+r_2^{-2})\cdot f^2/\sin^2\theta$. Obvious changes of variables to r_1, r_2, r_{12} can of course be made and the elliptic coordinates used by Hylleraas can be introduced here with the same boundary conditions.

Only P terms have been considered here. It is clear, however, that the same can be done for any other value of l. Since closed expressions for the general case are complicated, we do not consider them here.

Appendix

(I) Derivation of equation (4)

This can be derived either by the analytical procedure indicated in the text or else by the following geometrical consideration. The first three terms in (2) are squares of infinitesimal rotation operators about the axes x, y, z. The changes in ψ during a rotation are brought about

only through its dependence on θ', ϕ', ϕ. We draw two lines ON, OM in the xy plane with azimuths $-\pi/2+\phi$, ϕ. Resolving a rotation about OX along ON and OM with $ON \perp OM$ the first contributes $\sin\phi'\,\partial/\partial\theta'$. The second must be compounded as a sum of rotations along OZ and 0(1) and give rise to

$$\cos\phi'(\cot\theta'(\partial/\partial\phi')-(\partial/\sin\theta'\partial\phi))$$

The rotation operators are thus found to be

$$L_x=\sin\phi'\frac{\partial}{\partial\theta'}+\cos\phi'\left(\cot\theta'\frac{\partial}{\partial\phi'}-\frac{\partial}{\sin\theta'\partial\phi}\right).$$

$$L_y=-\cos\phi'\frac{\partial}{\partial\theta'}+\sin\phi'\left(\cot\theta'\frac{\partial}{\partial\phi'}-\frac{\partial}{\sin\theta'\partial\phi}\right)$$

$$L_z=\frac{\partial}{\partial\phi'}.$$

Equation (4) is then obtained as

$$[L_x^2+L_y^2+L_z^2+l(l+1)]\psi=0.$$

Usual commutation relations between rotation operators are of course also satisfied by L_x, L_y, L_z.

(II) Derivation of (16) and (24).

On account of spherical symmetry it is sufficient to calculate the variational equation for

$$\psi=F_1-F_2\cos\theta=a\cos\theta'+b\sin\theta'\cos\phi$$

where

$$a=F_1-F_2\cos\theta,\quad b=F_2\sin\theta.$$

The equation to be transformed is (23). The volume element is

$$dx_1\cdots dz_2=r_1^2r_2^2\sin\theta\sin\theta'dr_1dr_2d\theta d\theta'd\phi d\phi'.$$

We have

$$(\mathrm{grad}_1\psi)^2=\left(\frac{\partial\psi}{\partial r_1}\right)^2+r_1^{-2}\left[\left(\frac{\partial\psi}{\partial\theta_1}\right)^2+(\sin\theta_1)^{-2}\left(\frac{\partial\psi}{\partial\phi_1}\right)^2\right]$$

$$\frac{\partial\psi}{\partial\theta_1}=-F_1\sin\theta_1+\left(\frac{\partial F_1}{\partial\theta}\cos\theta_1-\frac{\partial F_2}{\partial\theta}\cos\theta_2\right)\frac{\partial\theta}{\partial\theta_1}$$

$$\frac{\partial\psi}{\partial\phi_1}=\left(\frac{\partial F_1}{\partial\theta}\cos\theta_1-\frac{\partial F_2}{\partial\theta}\cos\theta_2\right)\frac{\partial\theta}{\partial\phi_1}.$$

Remembering now that

$$\left(\frac{\partial\theta}{\partial\theta_1}\right)^2+\frac{1}{\sin^2\theta_1}\left(\frac{\partial\theta}{\partial\phi_1}\right)^2=1 \tag{a}$$

we have:

$$\left(\frac{\partial\psi}{\partial\theta_1}\right)^2+\frac{1}{\sin^2\theta_1}\left(\frac{\partial\psi}{\partial\phi_1}\right)^2=F_1^2\sin^2\theta_1+\left(\frac{\partial F_1}{\partial\theta}\cos\theta_1-\frac{\partial F_2}{\partial\theta}\cos\theta_2\right)^2$$

$$-2F_1\sin\theta_1\frac{\partial\theta}{\partial\theta_1}\left(\frac{\partial F_1}{\partial\theta}\cos\theta_1-\frac{\partial F_2}{\partial\theta}\cos\theta_2\right).$$

Substituting the value for $\partial\theta/\partial\theta_1$ which follows from the first equation (3) and using the second equation (3)

$$\sin\theta_1\frac{\partial\theta}{\partial\theta_1}=-\sin\theta'\cos\phi$$

Writing further

$$a'=\frac{\partial F_1}{\partial\theta}-\frac{\partial F_2}{\partial\vartheta}\cos\theta,\qquad b'=\frac{\partial F_2}{\partial\theta}\sin\theta$$

we transform the above expression into:

$$F_1^2\sin^2\theta'+(a'\cos\theta'+b'\sin\theta'\cos\phi)^2+2F_1(a'\cos\theta'+b'\sin\theta'\cos\phi)\sin\theta'\cos\phi.$$

Hence

$$\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} r_1^{-2}\left[\left(\frac{\partial\psi}{\partial\theta_1}\right)^2+(\sin\theta_1)^{-2}\left(\frac{\partial\psi}{\partial\phi_1}\right)^2\right]\sin\theta'd\theta'd\phi'd\phi$$

$$=\frac{(4\pi)^2}{3r_1^2}\left[F_1^2+(1/2)(a'^2+b'^2)+b'F_1\right].$$

Using the symmetrical expression for the term in r_2^{-2} and replacing all integrals of $(a\cos\theta'+b\sin\theta'\cos\phi)^2$ by $(4\pi^2/6)\,(a^2+b^2)$ equation (24) follows at once.

To verify (16) directly we evaluate

$$\frac{\partial^2\psi}{\partial\theta_1^2}+\cot\theta_1\frac{\partial\psi}{\partial\theta_1}+\frac{\partial^2\psi}{\sin^2\theta_1\partial\phi_1^2}\cdot$$

Remembering that

$$\left(\frac{\partial^2}{\partial\theta_1^2}+\cot\theta_1\frac{\partial}{\partial\theta_1}+\frac{\partial^2}{\sin^2\theta_1\partial\phi_1^2}\right)\theta=\cot\theta$$

and the relation (a), the above expression reduces to

$$\cos\theta_1\left[\frac{\partial^2F_1}{\partial\theta^2}+3\cot\theta\frac{\partial F_1}{\partial\theta}-2F_1\right]-\cos\theta_2\left[\frac{\partial^2F_2}{\partial\theta^2}+\cot\theta\frac{\partial F_2}{\partial\theta}+\frac{2\partial F_1}{\sin\theta\partial\theta}\right]$$

similarly for

$$\frac{\partial^2}{\partial\theta_2^2}+\cot\theta_2\frac{\partial}{\partial\theta_2}+\frac{\partial^2}{\sin^2\theta_2\partial\phi_2^2}\cdot$$

Substituting into Schroedinger's equation, (16) follows on requiring independent vanishing of coefficients of $\cos\theta_1$, $\cos\theta_2$.

AN INTERPRETATION OF PAULI'S EXCLUSION PRINCIPLE

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Abstract

I. Pauli's exclusion principle can be understood as an instance of the subjectivity of our knowledge. We are built out of only a particular world constructed according to one of the non-combining patterns possible under the laws of quantum mechanics. Therefore we are capable of having sense perceptions of only that world.

II. Dirac's theory of the proton shows why Pauli's principle governs the world.

I.

PROBABLY the most important trend in current physics is that toward the recognition of the fact that our science gives no information about an objective reality wholly independent of ourselves. We are becoming increasingly impressed by the subjectivity of our knowledge. We owe much of this to the work of Bridgman with his emphasis on the unprofitableness of dallying over meaningless questions and his operational formulation of the reality of physical concepts. The rôle played by our subjective limitations on observation of the world about us has been discussed in detail by Heisenberg and by Bohr. We refer to the train of ideas known as Heisenberg's uncertainty principle.

Let us consider what the uncertainty principle did for physics. It came after the fairly complete formulation of the laws of quantum mechanics as we know them to-day. Before the principle the laws were quite definitely stated by Heisenberg, Born, Dirac, Jordan, Schrödinger, Pauli and others. They were stated so definitely that the method of treating special problems was recognised and applied with a good deal of success by a large number of physicists. Therefore, they were valid laws of science, since they met the test of being workable in the hands of physicists in general, and did not rest purely on the genius of the individuals who discovered them. Even without the principle they probably could have attained a universal applicability but we cannot say how that would have been, since, owing to the slowness of diffusion of scientific knowledge, the formal laws were still in the process of becoming the common property of professional physicists when Heisenberg enunciated the principle.

But before he did, even among those who had found the new methods workable and who had contributed to the many successes of the theory, there was a feeling of dissatisfaction, a feeling that the new theory was not understood, perhaps even not understandable. These were disturbing times for we

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did not know why we felt dissatisfied (or perhaps unsatisfied) and so were quite helpless in attempting to remedy the situation. The remedy was provided by Heisenberg in his uncertainty principle. In a sense his famous paper in *Zeitschrift für Physik*, volume 43, has nothing new in it. For it does not alter or add to the formal statement of the laws of quantum mechanics. Nor does it apply them to any specific problem and produce calculations about some aspect of nature which are triumphantly in agreement with somebody's quantitative measurements. What it did do was to relieve that feeling of dissatisfaction. Many a physicist who had been working with the formalism of quantum mechanics felt that he understood it for the first time after he read that paper. Subsequently this satisfaction of understanding was considerably enhanced by the appearance of Bohr's Como lecture simultaneously in *Nature* and *Die Naturwissenschaften*. The title of Heisenberg's paper is significant: he called it the "anschaulich Inhalt" of the new quantum mechanics. It was just that: it was the intuitive, clear, evident content of the theory.

The important feature of this clear and intuitive part of the theory is the deflation of the lords-of-creation attitude of physicists. Wholly rational, detached fellows we thought ourselves (in our naive way), studying objectively the true laws of the external world. We had no concern with unfruitful stuff like metaphysics. Now we know otherwise and are healthily aware of our own organic relation to the traditionally inorganic subject matter of our science.

At present there is another law of nature (empirical, like all laws of nature) intimately connected with quantum mechanics, which we feel that we do not understand. This is Pauli's exclusion principle. We refer to the same feeling of dissatisfaction which was felt about quantum mechanics in general before Heisenberg's paper.

Pauli's principle grew out of empirical spectroscopy and was stated in the form that no two electrons in an atom can have the same set of quantum numbers. A formal place was found for this in the equations of quantum mechanics by Heisenberg, Dirac, Wigner and others. The equations of quantum mechanics showed a remarkable property when applied to the description of a dynamical system consisting of several dynamically similar particles. Such properties are naturally of fundamental importance because of the belief that all electrons are dynamically similar and that they are the fundamental stuff of which all substance is built. This remarkable property may be described by saying that such dynamical systems may exist in $N!$ different classes of states such that if the system exists now in one of these classes then it must exist for all time to come in this same class of states. (N is the number of similar particles in the system.) In other words, quantum mechanics provides, when applied to the dynamical system which is the entire universe, not just one solution but $N!$ possible solutions, which we may call worlds, where N is the total number of electrons in the universe. Since it is an exact conclusion from the postulated exact similarity of all the particles that the universe cannot change from one of these classes of states to

another, our universe must represent a selection from among these possible worlds. Which one? There is one which has the property that it has no possible states characterized by two of the particles' having the same quantum numbers. That one agrees with the world that we know.

That is fine but it leaves us with a lack of understanding of the matter which is, perhaps, akin to the unsatisfied feeling toward quantum mechanics which preceded the discovery of its "anschaulich Inhalt" by Heisenberg. What of the other $N!-1$ possible worlds?

Now we come to our main thesis: The restriction to a world built in accordance with Pauli's principle can be understood as another and extreme instance of the subjectivity of our knowledge. We, physicists, humans, are creatures who are built out of, and therefore are capable of reacting with and having sense perceptions of, only a particular world constructed according to a particular one of the non-combining patterns possible under the laws of quantum mechanics. Because of our own nature we are aware of, or conscious of, only that part of possible reality that is built on our pattern.

Do worlds really exist that are built (of the same electrons as ours) on one of the other patterns but nevertheless according to the laws of quantum mechanics? The question is meaningless in a sense because of our subjective incapacity to be aware of them. It is meaningless for the same reason as is the question, (sometimes asked after an individual has heard, for the first time, an exposition of Heisenberg's uncertainty principle) "Does a particle really have precise position and momentum simultaneously even though we cannot be experimentally aware of precise values for them?"

The situation turns on the meaning to be ascribed to the word "really" in the two questions. We prefer to associate with it the connotation, within the power of human sense perceptions. In that case the answer to both of them is no, as the "even though" clause makes ridiculously self-evident in the case of the second one. But we are reluctant to dismiss the other possible worlds quite so readily as we do simultaneous position and momentum. This is because the other worlds correspond to solutions of the equations of quantum mechanics, whereas there is no place in the structure of the mathematical formalism of quantum mechanics for simultaneous exact position and momentum.

Objective reality these other worlds cannot have, because of our subjective inability to react to them. (Remember that all objective reality is colored by important subjective elements!) This we feel is the simple, evident substratum of the Pauli exclusion principle which provides us with the right to say we "understand" it.

II

The foregoing shows that we can be conscious of only one of the possible worlds. But it throws no light on a possible reason why the real one is the one which obeys Pauli's exclusion principle.

One feels that the type of symmetry represented in our world is especially simple and that there must be some reason for it. It is another instance of an

ancient paradox: out of $N!$ possibilities the chance of the Pauli principle world being the real one seems vanishingly small. But in the matter of building the real world the dice are cast but once and in that one throw the antisymmetric pattern has an equal chance with the others.

Dirac's recent theory of the proton published in the Proceedings of the Royal Society for January, 1930, throws new light on the matter, however. When we spoke in *I* of there being $N!$ different possible worlds according to quantum mechanics, we were speaking of the non-relativistic theory. But the relativistic theory of the electron must represent a surer foundation on which to build cosmologic hypotheses. According to it, electrons can exist in states of negative energy (less than $-mc^2$), as well as in usual states of positive energy (of the order $+mc^2$). We have no experimental evidence of electrons of this sort and so the prediction of such negative energy electrons was regarded as a blemish in the theory. But now the solution to the difficulty is seen in the fact that Pauli's principle governs our world.

We can do no better than quote the crucial paragraph of Dirac's paper:

"The most stable states for an electron (i.e. the states of lowest energy) are those with negative energy and very high velocity. All the electrons in the world will tend to fall into these states with emission of radiation. The Pauli exclusion principle, however, will come into play and prevent more than one electron going into any one state. Let us assume that there are so many electrons in the world that all the most stable states are occupied, or, more accurately, that *all the states of negative energy are occupied except perhaps a few of small velocity*. Any electrons with positive energy will now have very little chance of jumping into negative-energy states and will therefore behave like electrons are observed to behave in the laboratory. We shall have an infinite number of electrons in negative-energy states, and indeed an infinite number per unit volume all over the world, but if their distribution is exactly uniform we should expect them to be completely unobservable. Only the small departures from exact uniformity, brought about by some of the negative-energy states being unoccupied, can we hope to observe."

And now we see why it is that the Pauli principle world is the only one which can be built out of Dirac's relativistic electrons. For it is the only one in which the available states can be filled up. For the others there is no limit to the number of electrons that can occupy a state. The antisymmetric one is the only pattern that has a "bottom." For the others all the electrons in the universe would be drained off into states of indefinitely great negative energy.

THE X-RAY SCATTERING POWERS OF NICKEL AND OXYGEN IN NICKEL OXIDE

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Abstract

Atomic F-curves for the nickel and oxygen atoms in NiO have been obtained from measurements of the intensities of the principal powder reflections of molybdenum, copper and nickel $K\alpha$ radiations. Though the scattering power of oxygen remains nearly constant with respect to NaCl for these wave-lengths, that of nickel shows important variations.

THIS paper forms part of a series of studies of the dependence of the diffracting power of an atom upon the wave-length of the x-rays being scattered. Accurate measurement[1] has shown that with wave-lengths as near together as the $K\alpha$ lines of molybdenum and rhodium the F-values of NaCl are equal for the same $\sin\theta/\lambda$. There is likewise some indication[2] that the atoms in this crystal do not have very different scattering powers for copper radiation. Recent comparisons of NaCl and metallic silicon[3] prove that the ratio of their diffracting powers is nearly the same for molybdenum and for copper $K\alpha$ x-rays. All of these observations are with radiations far removed in frequency from any critical values for the diffracting atoms.

Such a parallelism as that prevailing between NaCl and silicon no longer seems to hold if the comparisons involve metallic copper and iron reflecting molybdenum and copper rays. The experiments already made[4] with these metals indicate that their scattering powers decrease more rapidly with increasing wave-length than do those of the atoms of NaCl. This conclusion is dependent upon the essential correctness of measured absorption coefficients.

Observations upon NiO avoid such an uncertainty by containing within themselves a comparison of the scattering powers of two atoms—nickel and oxygen. These data consist of determinations of the F-curves of nickel and oxygen using molybdenum, copper and nickel $K\alpha$ radiation. The measurements upon which they are based are spectrometer studies of the intensities of the principal x-ray reflections of powdered NiO. The methods used in obtaining these intensities[5] and reducing them to atomic scattering powers have been described.

[1] R. W. James and E. M. Firth, Proc. Roy. Soc. **117A**, 62 (1927).
[2] E. Wagner and H. Kulenkampff, Ann. d. Physik **68**, 369 (1922).
[3] R. W. G. Wyckoff, Zeit. f. Krist. in press (1930).
[4] A. H. Armstrong, Phys. Rev. **34**, 931 (1929).
[5] A. H. Compton, X-rays and Electrons (New York, 1926) Chap. V; R. W. G. Wyckoff and A. H. Armstrong, Zeit. f. Krist. **72**, 319 (1929).

Two different samples of chemically pure green NiO gave results which were identical within the limit of experimental error. In order to suppress the effects of extinction both crystal powders were ground thoroughly in an agate mortar and passed through a 325 mesh per linear inch sieve before being formed into a cake.

Molybdenum radiation was obtained from a water-cooled General Electric tube operated from a synchronous motor-generator-kenetron-condenser

TABLE I. *The relative intensities of powder reflections of nickel oxide.*

Indices	Intensities for $K\alpha$ wave-length of Molybdenum	Copper	Nickel
111	111.8	112.4	129.7
200	159.4	196.1	207.3
220	[100]	[100]	[100]
113	48.9	36.4	42.2
222	29.1	26.4	28.3
400	13.4	10.7	—
133	19.1	—	—
240	28.8	—	—
224	20.5	—	—
333,115	12.5	—	—

set at 30 kv with a current consumption of 5 or 10 ma. The copper and nickel radiations were supplied by Siemens-Phoenix tubes passing 6 ma at 25 kv. The molybdenum rays were rendered essentially monochromatic with a ZrO_2 screen. No attempt was made to filter the x-rays emitted by the copper and nickel target tubes but calculation showed that with the resolution used none of the measured $K\alpha$ spectra was contaminated by other reflections.

TABLE II. *The F-values of powder reflections of nickel oxide.*

Indices	$\sin\theta/\lambda$	F(Mo $K\alpha$)	F(Cu $K\alpha$)	F(Ni $K\alpha$)
111	0.2076	14.13	11.41	13.01
200	.2398	22.60	20.56	22.52
220	.3391	18.28	15.83	16.88
113	.3976	10.76	8.13	9.16
222	.4153	15.12	12.52	13.43
400	.4796	13.65	10.12	—
133	.5223	9.22	—	—
240	.5359	11.65	—	—
224	.5871	10.96	—	—
333,115	.6229	7.96	—	—

The crystal structure of NiO is identical with that of NaCl. Reflections with odd indices therefore represent differences between the contributions of nickel and oxygen atoms, those with even indices (all even order spectra) are due to the cooperation of these two atoms. The relative intensities of the observed reflections for Ni $K\alpha$, Cu $K\alpha$ and Mo $K\alpha$ rays are shown in Table I.

The absolute F-values for molybdenum radiation have been found by comparing the (200) reflection of NiO with (220) of NaCl. A mean of several

determinations using both samples of NiO gave (200)NiO:(220)NaCl = 49.6:100. The apparent accuracy of this ratio is better than 5 percent. The mass absorption coefficient of NiO according to the experiments of Windgardh[6] is $\mu/\rho = 37.93$. If Allen's[7] value for nickel is used, μ/ρ becomes 37.21. The absorption coefficient of NaCl as provided by Windgardh's data is $\mu = 18.21$ ($\rho = 2.16$). Of the other quantities[8] needed to calculate absolute F's, ρ has been taken as 6.75, $a_0(\text{NiO}) = 4.17A$, $a_0(\text{NaCl}) = 5.628A$, $F(220, \text{NaCl}) = 15.62$. Introduction of these values into the customary expressions leads to the reflection F's recorded in Table II and Fig. 1. Points on the smooth F-curves drawn through them, when separated by addition and subtraction into

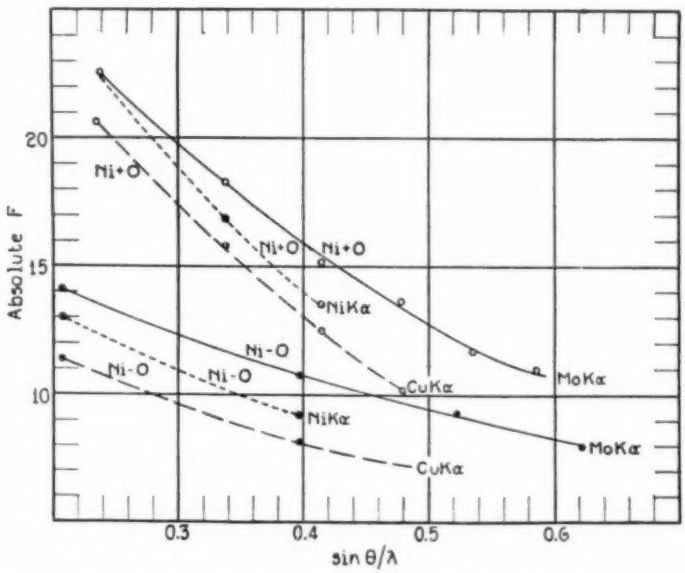

Fig. 1. The reflection F-values observed from NiO using molybdenum, copper and nickel $K\alpha$ radiations.

atomic F-values for nickel and oxygen, give the numbers listed in Tables III and IV and plotted in Fig. 2.

In order to place the F-curves for copper and nickel radiation upon an "absolute" scale for comparison with those for molybdenum x-rays, it has been assumed that $F(220, \text{NaCl}) = 15.62$ for all three radiations. The absorption coefficients for NiO as calculated by Jönsson's formula[9] are $\mu = 276.8$ for Cu $K\alpha$ and $\mu = 345.1$ for Ni $K\alpha$. They are in good agreement with existing experimental values. Absorption coefficients for NaCl obtained in the same way are $\mu = 161.2$ for Cu $K\alpha$ and $\mu = 196.2$ for Ni $K\alpha$. Measurements of the

[6] K. A. Windgardh, Zeits. f. Physik **8**, 363 (1922).

[7] S. J. M. Allen, Phys. Rev. **28**, 907 (1926).

[8] Internat. Critical Tables (New York, 1926) Vol. I p. 343; R. W. James and E. M. Firth, op. cit.

[9] E. Jönsson, Uppsala Univers. Årsskrift (1928).

relative intensities of (220) NaCl and (220) NiO have led to the ratios (220)NiO:(220)NaCl=100:57.5 for Cu $K\alpha$ and (220)NiO:(220)NaCl=100:51.8 for Ni $K\alpha$. The reflection F's calculated from these data are recorded

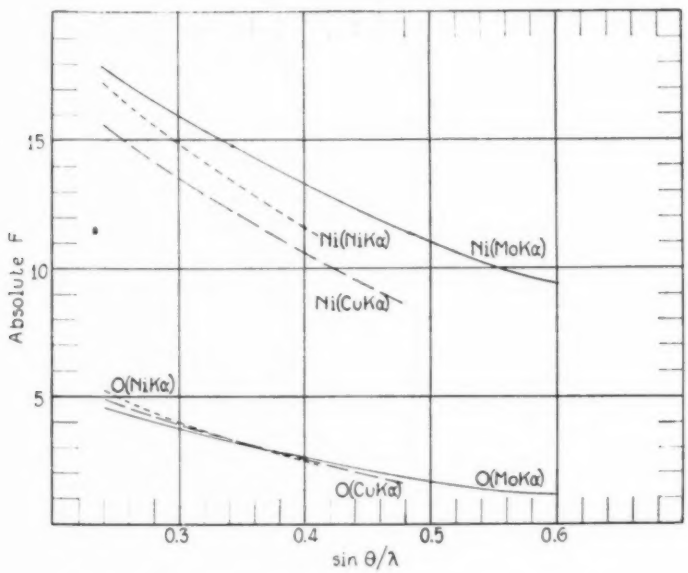

Fig. 2. The F-curves of nickel and oxygen atoms in NiO.

in Table II and plotted in Fig. 1. The atomic F's derived from them are listed in Tables III and IV and shown graphically in Fig. 2.

TABLE III. *Atomic F-values of oxygen in nickel oxide.*

sin θ/λ	F(Mo $K\alpha$)	F(Cu $K\alpha$)	F(Ni $K\alpha$)
0.240	4.55	4.87	5.23
.270	4.14	4.42	4.62
.300	3.77	3.96	4.06
.330	3.42	3.52	3.52
.360	3.05	3.10	3.05
.390	2.72	2.67	2.58
.420	2.39	2.27	2.30
.450	2.09	(1.87)	—
.480	1.81	(1.53)	—
.510	1.57	—	—
.540	1.35	—	—
.570	1.22	—	—
.600	1.15	—	—

Note: Values in parentheses in this and the following table are obtained by extrapolating the Ni-O curve of Fig. 1.

A check upon the accuracy of the measurements of this paper can be had by comparing the oxygen F-curves for Mo $K\alpha$ from NiO and[10] MgO. Though

[10] R. W. G. Wyckoff and A. H. Armstrong, Zeits. f. Krist. **72**, 433 (1930).

it is scarcely to be expected that they should be identical, these two curves ought to lie close to one another (Fig. 3).

The most significant feature of these results is the fact that though the oxygen *F*-curves are nearly identical for the three radiations—or, more accurately, vary in the same manner as does NaCl—relatively large differences exist in the curves for the nickel atoms. Since critical wave-lengths of oxygen

TABLE IV. *Atomic F-values of nickel in nickel oxide.*

sin θ/λ	F(Mo $K\alpha$)	F(Cu $K\alpha$)	F(Ni $K\alpha$)
0.240	17.95	15.62	17.37
.270	16.94	14.55	16.07
.300	16.03	13.57	14.87
.330	15.16	12.62	13.78
.360	14.33	11.72	12.81
.390	13.54	10.88	11.90
.420	12.79	10.04	11.37
.450	12.09	(9.25)	—
.480	11.41	(8.55)	—
.510	10.81	—	—
.540	10.25	—	—
.570	9.76	—	—
.600	9.39	—	—

are farther from the wave-lengths used than are those of NaCl, the observed slight increase in the oxygen *F*-curves at low angles with increasing wave-lengths is not contrary to expectation. The *F*-curves of nickel, lower for copper than for molybdenum radiation, agree with existing data upon copper[4] and iron in indicating that for atoms having critical frequencies within the experimental range, coherent scattering decreases with increasing wave-

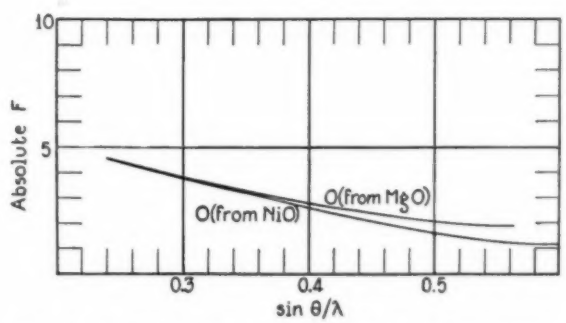

Fig. 3. A comparison of the oxygen *F*-curves for Mo $K\alpha$ rays as measured in MgO and NiO.

length as this critical range is approached. The greater diffraction of nickel for the nickel than for the copper $K\alpha$ line indicates that this downward trend is broken either some time before or when a wave-length characteristic of the scatterer is reached.

Further experiments are being made with various metals and with several wave-lengths which will bear upon these phenomena.

THE EFFECT OF HYPERFINE STRUCTURE DUE TO NUCLEAR SPIN ON POLARIZATION OF RESONANCE RADIATION

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(Received February 6, 1930)

Abstract

The existence of hyperfine structure must be taken into account in calculations of the polarization of resonance radiation based upon Heinsenberg's extension of the principle of spectroscopic stability. Where the hyperfine structures are due to the existence of a nuclear moment their effect upon the polarization of resonance radiation may be calculated. If the nuclear moment of the thallium atom is $\frac{1}{2}$ (in units of $h/2\pi$) as Schüler and Brück suppose the λλ3776 and 5350 lines should show no polarization, while λ2768 should show 33.3 to 35.1 percent parallel and λ3530 41.8 to 48.8 percent perpendicular to the electric vector of a plane polarized exciting beam. Sodium resonance radiation excited by plane polarized D_1 and D_2 lines should show 33.3 percent polarization if the nuclear moment is $\frac{1}{2}$ and 16.6 percent if it is 1. The latter value agrees well with 16.3 observed by the writer, but observations on band spectra seem to indicate a higher nuclear moment, according to F. W. Loomis and R. S. Mulliken (Verbal communication to the writer.)

THE success of Back and Goudsmidt[1] in accounting for the hyperfine structure and Zeeman effect of the Bismuth arc spectrum by ascribing a mechanical and magnetic moment to the nucleus of the atom has led to attempts to explain hyperfine structure found in various other spectra in the same manner. Schüler and Brück[2] have shown that the hyperfine structures of the TlI spectrum are probably due to a nuclear moment of $\frac{1}{2}$ (in units of $h/2\pi$) and McLennan, McLay, and Crawford[3] have shown that their observations on Tl II lend support to this hypothesis. More recently Schüler and Brück[4] have had some success in unraveling the hyperfine structures of Cd I by supposing that this spectrum is really two superimposed—one without hyperfine structure due to the cadmium isotopes of even atomic number which are supposed to have no nuclear moment, and another with structure due to a nuclear moment ascribed to the odd isotopes.[5] The idea of nuclear spin has been used also by Jackson[6] and by Hargreaves[7] to account for Jackson's observations on the hyperfine structure of Cs I.

[1] Back and Goudsmidt, Zeits. f. Physik **43**, 321 (1927); **47**, 174 (1928). Pauli, Naturwiss. **12**, 741 (1924) suggested the idea of nuclear spin, but it was not successfully applied to the explanation of hyperfine structures until the paper of Back and Goudsmidt.

[2] Schüler and Brück, Zeits. f. Physik **55**, 575 (1929).

[3] McLennan, McLay and Crawford, Proc. R S **A125**, 570 (1929).

[4] Schüler and Brück, Zeits. f. Physik **56**, 291 (1929).

[5] Goudsmidt, Naturwiss. **41**, 805 (1929).

[6] Jackson, Proc. Roy. Soc. **A121**, 805 (1929).

[7] Hargreaves, Proc. Roy Soc. **A124**, 568 (1929).

That the existence of hyperfine structures must be taken into account in any comparison of theory and experiment on the polarization of resonance radiation or of radiation excited by electron impact is obvious for the calculation of the polarization in the absence of a magnetic field, based on the idea of spectroscopic stability,[8] involves the relative intensities of the Zeeman components of the line in *very weak* fields.

All previous calculations of the polarization of resonance radiation have been carried out without taking into account the existence of hyperfine structure. The Zeeman patterns and transition probabilities used have been those calculated for an atomic model without nuclear spin. These intensities are, at least to a first approximation, those which will obtain when the Paschen Back effect of the *hyperfine structure* is complete. There is no reason to expect that calculations made on this basis will show good agreement with experiment and in fact the agreement in general is poor. That hyperfine-structure is responsible for the 80 percent polarization of the λ2537 A. U. resonance radiation of mercury has been shown experimentally by MacNair and the writer.[9]

It is not likely that the hyperfine structure of this line is to be accounted for on the hypothesis of nuclear spin alone but in the case of thallium and perhaps sodium the situation is different, and it is interesting to see whether taking into account the nuclear spin will lead to better agreement between theory and experiment.

The present calculations are based on the assumption that the coupling between i, J, and f is of the same character as that between L, S and J in alkali spectra. That is, it is supposed that i, the nuclear moment, combines vectorially with J, the net moment due to the remainder of the atom to give a resultant f in the same way that L and S combine to give a resultant J. This is the assumption used by Back and Goudsmidt[1] and by Schüler and Brück.[2,4] The relative intensities of the hyperfine lines making up a hyperfine structure pattern (which itself appears as a 'line' save under high revolving power) may be calculated by formulas given by Hill[10] and by Hargreaves.[7] The relative intensities of the Zeeman components of the hyperfine lines may be calculated by the usual Kronig-Hönl formulas.[11] The polarization to be expected in any specified experiment is then calculated by making use of a consequence of the principle of spectroscopic stability first enunciated by Heisenberg.[8] This extension of the principle of spectroscopic stability may be applied in any case where the experimental situation presents an axis of symmetry, and it states specifically that the introduction of a magnetic field parallel to this axis will not alter the relative probabilities of transitions giving rise to radiation polarized respectively parallel or perpendicular to this symmetry axis. The field is introduced merely to remove the degeneracy which exists in the absence of any field. That is, its purpose is to render

[8] Bohr, Naturwiss. **12**, 1115 (1924); Heisenberg, Zeits. f. Physik **31**, 617 (1926).
[9] MacNair and Ellett, Phys. Rev. **31**, 180 (1928).
[10] Hill Proc. Nat. Acad. Sci. **15**, 779 (1929).
[11] Kronig, Zeits. f. Physik **31**, 885 (1925); Hönl, Zeits. f. Physik **31**, 340 (1925).

distinct the various magnetic energy levels which coalesce in the absence of a field so that the relative probabilities of transitions between these levels may be calculated. While this hypothetical field must be a strong field in the sense that the degeneracy is removed completely it must at the same time be a weak field so far as the production of Paschen Back effect of the hyperfine structure is concerned. The justification of such procedure then requires that the separation between the various hyperfine structure components of a line should be large compared to the intrinsic breadth of these components. This intrinsic breadth has nothing to do with the breadth of lines as observed in high resolving power spectroscopes; the latter is due to Doppler effect and pressure broadening (collisions) etc. We refer here to the inherent breadth of the line occasioned by imperfect definition of energy levels resulting from the finite life of stationary states.

To calculate the polarization of resonance radiation excited by plane polarized exciting light in the absence of a magnetic field we must imagine a field introduced, its direction being that of the symmetry axis (here the electric vector of the exciting light) so that we may calculate the relative numbers of transitions to the several Zeeman levels into which the upper states involved are split. Then having calculated the relative populations of these levels we determine the relative numbers of return transitions giving rise to radiation polarized parallel or perpendicular to the field. From this we get the polarization of the reemitted radiation and are assured that the value so calculated is that which will obtain when the field is removed.

Thallium

The thallium lines arise from transitions shown in the Grotrian diagram, Fig. 1a. Each of the levels shown is split into two when a nuclear moment of $\frac{1}{2}$ is taken into account, and these with the appropriate values of the fine quantum number f, and the permitted transitions are given in Figs. 1b and 2. The values of the transition probabilities are given by Hargreaves[7]—or

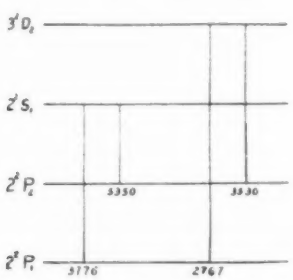

Fig. 1a. Grotrian diagram for thallium.

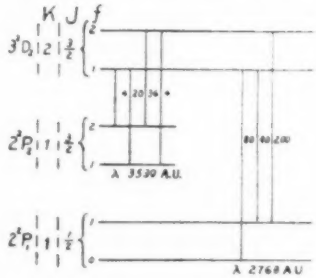

Fig. 1b. Permitted transitions in thallium.

they may be readily computed from the formulas given by Hill.[9] From the figures it is evident that excitation by λ3776 A. U. will give rise to the emission of this line and also λ5350 A. U. while absorbtion of λ2768 A. U. excites λ3530 A. U. in addition to itself. In Fig. 2 are shown the Zeeman levels and

transitions involved in the emission of λλ3776 and 5350 A. U. Excitation by plane polarized light will excite atoms to those upper energy levels reached by those transitions of λ3776 A. U. marked ‖ (parallel) in the figure, the relative numbers of excited atoms in the various upper states depending upon the values of the parallel transitions reaching it and upon the intensity of the incident light of wave-length appropriate to produce these transitions. The question of relative intensities in the exciting radiation need not bother us here however, for no matter what the relative populations of the upper levels the reemitted radiation of each of the aggregates of hyperfine lines composing λλ3776 and 5350 A. U. will be unpolarized. That is to say, in each of these aggregates from *each* upper level the chance of returning by a perpen-

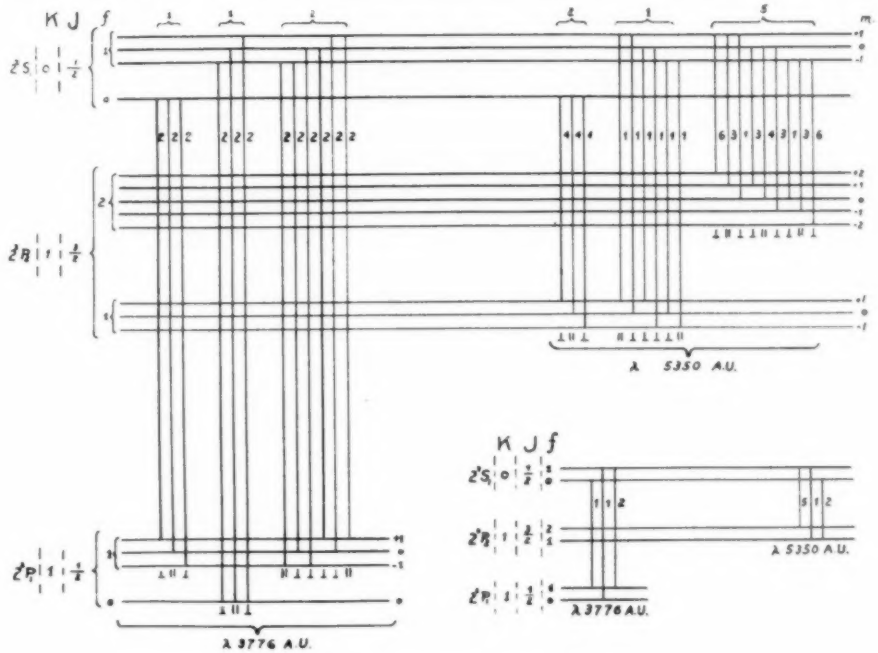

Fig. 2. Permitted transitions in thallium.

dicular transition is twice that of returning by a parallel transition. This leads to no net polarization either parallel or perpendicular to the electric vector of the exciting light—for parallel transitions produce such a distribution of the reemitted radiation as would be produced by a linear oscillator parallel to the electric vector of the exciting light (and also parallel to our imaginary magnetic field) while perpendicular transitions give rise to a distribution such as would be occasioned by a circular oscillator in a plane perperdicular to this.

Figure 3 shows the levels involved in absorption and emission of λλ2768 and 3530 A. U. Here the relative population of the upper levels is of some consequence and it becomes necessary to make some assumption regarding the distribution of intensity over the hyperfine structure components of

λ2768 A. U. Two cases will be considered —A— that of uniform intensity over the entire absorption pattern, a situation perhaps realizable with a very hot source emitting greatly broadened lines, and —B— that of the theoretical intensity ratios,—such as might be realized with a source run at a temperature low enough so that Doppler broadening will cause no overlap of

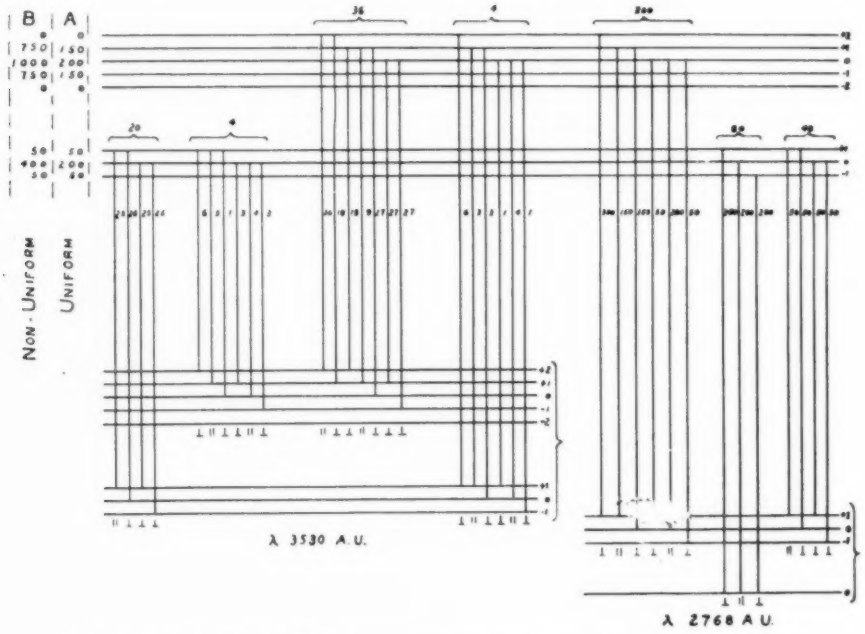

Fig. 3. Levels involved in absorption and emission of λλ2768 and 3530.

hyperfine structure components, and with the density of thallium vapor low enough to eliminate self reversal. In column A of Fig. 3 are given the relative populations of the upper levels for case A and in column B for case B. Table I summarizes the results for these four lines.

TABLE I.

Nuclear moment i	0	1/2		observed
		A	*B*	
2768	60 ∥	33.3 ∥	35.1 ∥	35 ∥ (500°C) 55 ∥ (470°C)[12a]
3530	75 ⊥	41.8 ⊥	48.8 ⊥	30 ⊥ (500°C) 60 ⊥ (470°C)[12a]
3776	0	0	0	0[12b]
5350	0	0	0	0[12b]

Observed values[12a,b] are given in column five, while the values to be expected for an atom without nuclear moment are given in column two.

More recently Schüler and Brück[13] have advanced the hypothesis that in

[12a] Gülke, Zeits. f. Physik **56**, 524 (1929).
[12b] Ellett, Nature **114**, 931 (1924).
[13] Schüler and Brück, Zeits. f. Physik **58**, 735 (1929).

thallium as well as cadmium[4] there is a difference of nuclear moments of the isotopes. The presence of an isotope having zero nuclear moment would result in higher values for the polarization, but the presence of such an isotope is not indicated by the spectroscopic data. An isotope with nuclear moment greater than one half probably would lead to even lower values of the expected polarization as a higher nuclear moment means an increased multiplicity of hyperfine structure levels. This might be offset by the changed intensity distribution in the exciting light, as it would be to some extent at least if the components of the hyperfine structure pattern responsible for the polarization should have the same wave-length in the patterns of both isotopes. Whether such a situation exists we cannot say without a more detailed spectroscopic analysis of the thallium hyperfine structures.

Sodium

For a sodium atom without nuclear moment resonance radiation excited by the D_2 line alone should be 60 percent polarized. When excited by D_1 and D_2 together, using a source such that the effective intensity ratio of the two lines is 2:1 (the theoretical value) the predicted polarization is 50 percent. In 1925 the writer found[14] 16.3 percent for the polarization of resonance radiation excited by both D lines, which corresponds to a value of 20.1 percent for D_2 alone not 24 percent as Datta states.[15] Datta, exciting by means D_2 alone got values as high as 33 percent with the resonating vapor in equilibrium with metallic sodium at 115°C. He supposed that the lower value obtained by the writer was due to higher vapor pressure. This however is not the explanation, for the vapor pressure was actually less than the lowest at which Datta made observations; 95°C and 7.4 10^{-8}mm. Hg[16] as against his values of 115°C and 4.5 10^{-7} mm Hg. More recently the experiment has been repeated with a somewhat more powerful source and vapor pressures as low as $1.9 \cdot 10^{-8}$ mm Hg (80°C). The polarization was again found to be 16.3 percent. The reason for the difference between this value and Datta's is not obvious to the writer.

Schüler[17] has observed hyperfine structure of the D lines, and as the hyperfine structure observed in caesium appears to be due to a nuclear moment, I have calculated the polarization to be expected in D line resonance radiation on the assumption of various nuclear moments. In every case the value is less than it is for the atom without nuclear moment. As the sodium hyperfine structure is on a very small scale it has been assumed that the intensity of the exciting light is uniform across the hyperfine structure pattern. This amounts to supposing that the separations in the pattern are small compared to the Doppler line breadth at the temperature of the source. The temperature of the glass walls of the source used by the writer was about 750°C and

[14] Ellett, Jour. Opt. Soc. Am. **10,** 427 (1925).

[15] Datta, Zeits. f. Physik, **37,** 625 (1926).

[16] Vapor pressures extrapolated from data of Rodebush and De Vries, Jour. Am. Chem. Soc. **47,** 2488 (1925).

[17] Schüler, Naturwiss. **16,** 512 (1928).

the emission lines have a corresponding breadth, as I have shown by experiments on polarization of resonance radiation in strong magnetic fields.[18]

The results of these calculations are summarized in Table II.

TABLE II.

i	0	1/2	1	obs.
D_2	60	40.54	20.5	33[14]
D_1	0	0	00	00
D_1+D_2	50	33.3	16.6	16.3[2]

In this connection it should be mentioned that observations of alternating intensities in sodium band spectra indicate a quite large nuclear moment,[18] probably greater than one, which probably would lead to even lower values for the polarization.

In conclusion it may be said the presence of hyperfine structure due to nuclear spin cannot be neglected in calculating the polarization of resonance radiation and radiation excited by electron impact. Taking account of such hyperfine structures in certain thallium and sodium lines leads to lower values of the predicted polarization and consequently better agreement between theory and experiment. Experiments on the polarization of resonance radiation may yield the data required for the solution of hyperfine structure problems in cases where direct spectroscopic analysis is impossible, as in the case of overlapping of certain components in the hyperfine structure patterns because of Doppler breadth of the lines.

[18] Ellett, Phys. Rev. **29**, 904 (1927).

[18] F. W. Loomis and R. S. Mulliken agree from inspection of Loomis spectrograms of Na_2 bands that i is probably 3/2 or greater. (Verbal statement to the writer). See also Loomis and Wood, Phys. Rev. **32**, 223 (1928).

SPECTROSCOPIC EVIDENCE OF TWO TYPES OF AMMONIA MOLECULE

By Joseph W. Ellis
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(Received February 3, 1930)

Abstract

A two-fold difference exists in the equations expressing the anharmonic frequencies arising from vibratory energy changes in ammonia molecules in solution and in gaseous form. The greater coefficient of the n^2 term in the former case, indicating a more rapid approach of the energy terms toward confluence, is assumed to arise from the proximity of the molecules of the solvent. The presence of a constant term of appreciable magnitude in the solution equation is interpreted as measuring the energy required to change the molecule from an α form to a β form of greater potential energy. Chemical support for this latter interpretation is sought in some earlier measurements by Baly and Duncan on the difference in the decomposition rates of ammonia both after immediate evaporation from the liquid and after it had stood for a considerable length of time.

It becomes easier to interpret the Raman spectrum of liquid ammonia, ammonia in aqueous solution and a liquid organic derivative of ammonia, aniline, when the existence of a constant in the infra-red formula is recognized.

BADGER and Mecke[1] and the author[2] have independently come to the conclusion that the ammonia molecule has a fundamental absorption wavelength near 3μ. This conclusion has been arrived at in each instance by the discovery that there is an anharmonic series of absorption bands with members in the infra-red spectrum below 3μ and in the visible spectrum. The former investigators have photographed the fourth and fifth members of this series in the visible region, using long tubes of gaseous ammonia and a concave diffraction grating to secure high dispersion and resolving power. Out of the complex structure caused by rotational quantum changes they have been able to pick the lines produced by vibrational energy changes alone. They have sought the second and third members in the thermal measurements of Robertson and Fox[3] and have used the frequency values of the centers of these unresolved bands. For the first member they have chosen the frequency of maximum absorption in the unresolved Q branch in the record given by Barker.[4] They have shown that these five frequencies can be fairly well fitted to the following anharmonic formula:

$$\nu_n = 3396n - 60n^2. \tag{1}$$

The author[2] has used a quartz prism spectrograph to photograph the structureless absorption bands corresponding to the fourth and fifth series

[1] Badger and Mecke, Zeits. f. Phys. Chem. B **5**, 333 (1929).
[2] Ellis, Journal Franklin Inst. **208**, 507 (1929).
[3] Robertson and Fox, Proc. Roy. Soc. **A120**, 128 (1928).
[4] Barker, Phys. Rev. **33**, 684 (1929).

members caused by ammonia in aqueous solution. In a similar manner he has also found the weak sixth member in the visible green spectrum. Records of the second and third members have been secured by means of a registering infra-red spectrograph equipped with a thermopile. These latter he has shown retain their positions when carbon tetrachloride replaces water as a solvent. No data for the solution were then available for the first member. For reasons explained in the above reference a wave-length value of 2.916μ was assigned to the initial member of the series.

Although the former reason for selecting this value does not now seem to be well founded, the wave-length value chosen has been shown to be at least approximately correct. To show this a Hilger D 35 infra-red spectrometer equipped with a rock-salt prism was used. A 1 cm cell of ammonia in carbon tetrachloride solution was placed before the slit of the instrument and observations were made on the 3μ region. The difficulty experienced by Robertson and Fox[3], namely that the wave-length determination of an absorption maximum is influenced by the variations in the refractive index of the rock-salt prism caused by temperature changes, was experienced here. When, for example, the wave-drum was set for a correct reading with the yellow sodium lines filling the thermopile slit and the instrument allowed to stand for a while with the lamp source radiating near by, the absorption band produced by a 1 mm cell of benzene shifted from its true position of 3.27μ to a value in excess of 3.4μ. Consequently, just prior to a determination of the position of the ammonia band, the reflecting mirror near the prism was so adjusted that when the galvanometer showed a miminum deflection, indicating that the maximum of absorption due to the benzene had been reached, the wave-drum indicated 3.27μ. With this procedure it was found that the ammonia solution band was not at 3.0μ, the position occupied by the gaseous ammonia band, but at 2.9μ.

The frequencies of the six members of the series observed in solution have been shown[2] accurately to fit the formula:

$$\nu_n = 97 + 3400n - 70n^2. \tag{2}$$

Now in spite of the assertion by Mecke[5] that there is a good agreement between the bands observed in gaseous ammonia and in solution, a closer examination reveals a significant difference. This difference is two-fold and is revealed in Eq. (2) by the presence of the constant term 97 and by the larger coefficient of the n^2 term, 70 as compared with 60 in Eq. (1). The presence of the constant term arises from the origination of the solution series at 2.9μ rather than at 3μ. The greater coefficient of the quadratic term explains why in the higher series members the wave-lengths of the solution bands become greater than the corresponding bands in the gas. This earlier confluence of the solution series must arise from a more rapid diminution of the force coefficient of the vibrator caused by the proximity of surrounding molecules. In general, however, a less rapid approach of the series members toward confluence would be expected, because this would

[5] Mecke, Trans. Faraday Soc. **25**, 942 (1929).

mean a lesser value for the heat of dissociation of the vibrator. And heats of dissociation evaluated from data obtained from the liquid state should be less than heats of dissociation evaluated from the gaseous state by an amount approximately equal to the heat of vaporization.

Fig. 1 is included to show the difference in the locations of the fifth members of the series in solution and in the gas. The figure shows the solution band approximately symmetrically located between two neon comparison lines, 0.6507μ and 0.6533μ. It has been given the value of 0.652μ. The value given by Mecke and Badger for the analogous gaseous band is 0.647μ, which lies completely outside of the region of absorption in the solution.

The constant term in Eq. (2) has been interpreted[2] as representing the amount of energy, in wave-number units, required to change the molecule in solution over to a new form before vibration takes place. A chemical investigation carried out a number of years ago by Baly and Duncan[6] seems to have some bearing upon this subject. These authors showed that

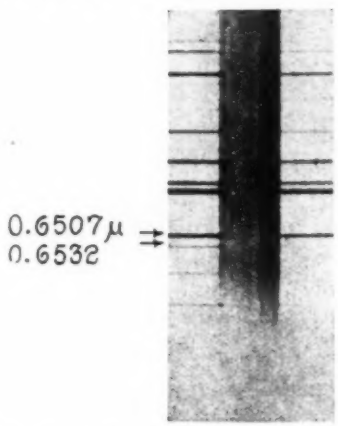

Fig. 1. The 0.652μ absorption band of ammonia in aqueous solution.

ammonia gas which had been slowly evaporated from the liquid or which had stood for some time in contact with the liquid had a certain constant rate of decomposition. The decomposition was effected by thermal energy supplied at a known rate by a heated platinum wire and the decomposition rate was determined from pressure changes in the gas. But when the experiment was repeated upon gas which had been suddenly evaporated from the liquid they found that the decomposition rate was much less than in the previous instance. Furthermore, this rate gradually increased with time. These facts led the investigators to postulate two forms of ammonia molecules, which they designated inactive and active forms, but which we shall designate as α and β forms respectively for reasons which will be apparent presently. The molecules are in the α form when the substance is in the liquid state or in the gaseous state immediately following sudden vaporization. The β form makes up predominantly, or exclusively, the gas which has stood

[6] Baly and Duncan, Jour. Chem. Soc. **121**, 1008 (1922).

for a considerable length of time. According to these investigators, the decomposition rate of inactive (α) ammonia is lessened because of the use of a portion of the energy supplied by the wire to activate the molecules.

Tronstad[7] has pointed out that the experimental procedure of Baly and Duncan was similar to that of Bonhoeffer and Harteck in their study of ortho and para hydrogen. He furthermore has stated that Baly and Duncan have not proved the existence of two chemically different types of ammonia molecules, but that their results can be explained equally well on the basis of two forms with different heat conductivities and specific heats. The two types would then be analogous respectively to para and ortho hydrogen.

From considerations of the experimental results of Baly and Duncan it may be concluded that the 97 cm^{-1} term of Eq. (2) represents an energy of "activation." (The assumption is made here that ammonia in solution exists in the α state.) However, in the light of Tronstad's criticism it must be recognized that this activating process may be one in which geometrical and physical changes occur rather than chemical changes.

From the quantitative measurements of Baly and Duncan it would seem that the modified interpretation of Tronstad is the more tenable. Baly and Duncan have shown that in some instances the amount of decomposition is doubled when the β form is used in place of the α form. Under their interpretation then half of the energy supplied by the hot platinum wire must go into energy of activation. Now the energy required to decompose one molecule of NH_3 into NH_2 and H requires some 30,000–40,000 cm^{-1} [2] which is 300 or 400 times as great as the 97 cm^{-1} energy of activation. But Baly and Duncan state that from 0.5 to 4 percent of the molecules are decomposed during the 20 seconds of observation; and under the assumption that this percentage of molecules decomposes, say into NH_2 and H, there would be required many more molecules than the total number available, to take up the energy of activation.

Following Tronstad's assumption of a greater heat conductivity characterizing the α molecules, the difficulty met with in the discussion of the above paragraph does not enter, for more of the heat than previously could escape to the surrounding constant temperature water bath.

It should be pointed out that Barker,[8] following Hund, has postulated two forms of ammonia molecule in his interpretation of the doubleness of another fundamental infra-red band of ammonia at 10.5μ. The difference in potential energy between the two types, however, is only 27 cm^{-1}. The approximate equality in intensity of the two components of this double band lead to the conclusion that the two kinds of molecules postulated must exist in the gaseous state with approximately equal abundance. Mecke[9] also believes that his visible bands which are harmonics of the 3μ fundamental also exhibit a double structure, one set being much weaker than the other. But the frequency difference which he finds is even lower than Barker's 27 cm^{-1}.

[7] Tronstad, Zeits. f. Phys. Chem. B **5,** 333 (1929).
[8] Barker, Phys. Rev. **33,** 684 (1929).
[9] Mecke, Phys. Zeits. **30,** 907 (1929).

The Raman spectrum of ammonia exhibits one, two or three lines corresponding to the 3μ region, the exact locations and number of components depending upon the phase in which the substance exists and upon the individual investigators. Wood[10] and Dickinson, Dillon and Rasetti[11] have shown that the Raman frequency corresponding to a rotationless vibrational energy change in the gaseous molecule is 3330 and 3334 cm^{-1} respectively, in good agreement with the 3336 cm^{-1} value obtained by putting n equal to 1 in Eq. (1). The latter investigators[11] have shown that liquid ammonia yields two frequencies, 3298 and 3214 cm^{-1}. Daure, [12] however, found in addition to these two frequencies, a third one at 3380 cm^{-1}. His record shows that all three components have approximately equal intensities.

Carrelli, Pringsheim and Rosen[13] found two frequencies, 3385 and 3312 cm^{-1}, when they used an aqueous solution of ammonia. These authors recognized, however, the possibility that one of these components may have been due to the water solvent.

If the three components found by Daure in the liquid all originate in ammonia molecules, they might be explained by assuming the existence of both the α and β forms of molecule in the liquid state. The components corresponding to greatest, intermediate and least frequency changes could then be correlated with the following energy changes respectively:—α, $0 \rightarrow \beta$, 1; α, $0 \rightarrow \alpha$, 1 or β, $0 \rightarrow \beta$, 1; and β, $0 \rightarrow \alpha$, 1. Here α, 0 designates a vibrationless α type of molecule, β, 1 a β type of molecule vibrating in quantum state 1, etc. The 80 and 90 cm^{-1} frequency differences between the components are comparable to the 97 cm^{-1} term of Eq. (2). However, the failure of Dickinson, Dillon and Rasetti completely to corroborate the findings of Daure raises the question as to whether impurities may have been present in the latter's experiment. Water would be the most likely impurity and water yields at least two Raman bands with frequencies comparable to those given.

Spectroscopically, aniline, $C_6H_5 \cdot NH_2$, which is a derivative of ammonia, behaves in a manner similar to its parent substance. The writer has justified his earlier correction[14] to Bell's[15] 2.8μ value for the fundamental N–H band, for he has studied the 3μ region for aniline with the Hilger D35 infra-red spectrometer and has found the band to have its maximum of absorption at 2.9μ. There is a remarkably close agreement between the members of the anharmonic series originating at 2.9μ for aniline and for ammonia in solution. Consequently, a constant term must be included in the aniline series, a fact which has hitherto[14] been overlooked.

Again, the Raman effect in aniline according to Bonino[16] shows a single frequency shift corresponding to a 3.0μ wave-length, rather than to 2.9μ. Thus once more the difference between the Raman frequency and the fundamental infra-red frequency is of the order of 97 cm^{-1}.

[10] Wood, Phil. Mag. **7,** 774 (1929).
[11] Dickinson, Dillon and Rasetti, Phys. Rev. **34,** 582 (1929).
[12] Daure, Thesis, Masson et Cie, Paris, (1929).
[13] Carrelli, Pringsheim and Rosen, Zeits. f. Phys. Chem. B **5,** 333 (1929).
[14] Ellis, Phys. Rev. **33,** 27 (1929).
[15] Bell, Jour. Amer. Chem. Soc. **47,** 2192 (1925).
[16] Bonino, Gazz, chim. Ital. **59,** 668 (1929).

THE AFTERGLOW IN AIR

By Joseph Kaplan
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Abstract

It was observed that on passing a weak discharge through the air glow the β bands of nitric oxide were very strongly excited. These bands possess several very interesting properties. They correspond to a transition from the B to the X level of the molecule and the transition $B_0 - X_0$ is very improbable because of the large difference in nuclear separation. These bands have never been reported as being intense in electric discharges and they have been obtained with considerable intensity only in active nitrogen. This present experiment is therefore the first one in which these bands have been observed with great intensity in an electric discharge. The β bands, as observed in the present experiments, correspond to transitions only from the B_0 to the various X vibrational levels, whereas in the afterglow of active nitrogen they correspond to transitions from several B levels to the various X levels. This difference indicates that there are at least two possible methods for exciting these unusual bands and they have been discussed in brief by Kinsey and the author. They are excitation by recombination, and excitation by collisions of the second kind.

Introduction

THE problem of afterglows has been attacked in a great many different, ways in recent years. Of the various afterglows that have been studied the one receiving the most attention has been the afterglow in active nitrogen. The reason for the widespread interest in active nitrogen is readily understood when one considers the many interesting phenomena that have been observed in connection with it. These extend from the field of excitation of spectra by active nitrogen to that of surface chemistry. And because of the large range of action of active nitrogen it has been interesting both as a tool and as a problem in itself. In the present communication it is proposed to discuss some aspects of a much less studied and apparently far less interesting afterglow. The afterglow referred to is the one that is observed when almost any type of discharge is passed through air at pressures around 0.5 mm.

This afterglow was first observed by E. P. Lewis[1] and also studied by R. J. Strutt[2] during those years in which he made many very valuable contributions to the problem of afterglows. The spectrum of the air glow has not been studied to any great extent and there are no published photographs of it. Herzberg,[3] and independently the author,[4] have photographed the spectrum of the glow and found it to be continuous. Herbzerg has reported a

[1] E. P. Lewis, Ann. d. Physik (4) **2,** 459 (1900).
[2] R. J. Strutt, Proc. Phys. Soc. **23,** 66 (1911).
[3] Herzberg, Zeits. f. Physik **46,** 878 (1927).
[4] Kaplan, Proc. Nat. Acad. Sciences **14,** 258 (1928).

maximum in the red and a decrease of intensity toward the violet. In addition to the continuous spectrum in the visible, the writer has reported the excitation of the OH band at 3064A. This band was undoubtedly excited by the active species in the afterglow, but as yet there is no basis for definitely discussing the process of excitation, since no experimental or theoretical work regarding the energy of the active species has appeared. Part of the purpose of the present work was to begin experiments designed for the purpose of studying in more detail than has been done, the nature of this afterglow.

Recently, Herzberg[3] and others have revived interest in the air glow by applying to its study a few of the methods that had been used in connection with the nitrogen afterglow. Herzberg has studied the effect of varying the relative amounts of oxygen and nitrogen in the discharge in which the afterglow was produced and also the influence of the condition of the walls of the containing-vessel. Other papers by Majewska,[5] Majewska and Witold[6] and Bernard Lewis[7] report work on the effect of surfaces, the rate of decay of the afterglow and on the mutual effects of nitrogen and oxygen on their afterglows. As the last title suggests, the continuous afterglow in air and in other mixtures of oxygen and nitrogen, has been ascribed to oxygen and several recent writers have suggested that it may simply be a recombination spectrum of atomic oxygen. It is not the purpose of this paper to discuss this point and it will be left for another communication. There is however no conclusive evidence in favor of the recombination hypothesis although the continuous spectrum makes that hypothesis a tempting one.

Another method of attack has recently been applied to the air afterglow by the author. The method, briefly, consists of allowing the active material to pass from the discharge in which it was formed into another discharge through which a very feeble current from a small spark coil is passing. The spectrum in the auxiliary tube is studied and the effect of the active material is noted. Recently Bay and Steiner[8] have applied this method to active hydrogen, active nitrogen and to a modification of oxygen to which they refer as active oxygen. They used external electrodes and electrodeless ring discharges whereas in the present experiments internal electrodes were used. The method was first used by the author in an attempt to excite atomic nitrogen lines in active nitrogen and it yielded some very interesting results. In the following a brief account will be given of some of the results of the present work.

Experimental Method

The afterglow was produced by passing an uncondensed discharge from a 1 kw Thordarsson transformer, giving 20,000 volts in the secondary, through various mixtures of oxygen and nitrogen. The pressure of the gas in the discharge was 0.5 mm and this has been found to be the best pressure

[5] Majewska, Zeits. f. Physik **50,** 372 (1928).
[6] Majewska and Witold, Zeits. f. Physik **48,** 137 (1928).
[7] B. Lewis, J.A.C.S. **51,** 654 (1929); B. Lewis, J.A.C.S. **51,** 665 (1929).
[8] Bay and Steiner, Zeits. f. Phys. Chemie **3,** 149 (1929).

for the production of the afterglow. It is interesting to note that 0.5 mm is also about the optimum pressure for the production of atomic hydrogen and active nitrogen. The active material was allowed to pass into another discharge tube, having internal electrodes, and a weak discharge from a small spark coil was allowed to pass through this tube. The spectrum of this discharge was photographed on a Hilger E2 spectrograph and also on a small Gaertner instrument. The auxiliary discharge was sufficiently weak as to make it necessary to expose for about ten hours on the Hilger instrument in order to obtain reasonably intense plates. It is apparently the weakness of the auxiliary discharge that makes the method a valuable one in the study of active materials from discharges.

Experimental Results

Several interesting results were obtained but the only one that is to be here discussed is the excitation of the β bands of nitric oxide. A preliminary note on these results was published in the letter column of the Physical Review.[9] The excitation of these bands with considerable intensity was certainly the most striking effect of the introduction of the active material into the weak discharge. The β bands are of special interest first because they have been obtained with considerable intensity only in the nitrogen afterglow and secondly, because of the large change in moment of inertia between the two levels that are involved in the excitation of these bands.

The β bands were first obtained by E. P. Lewis[10] in active nitrogen. The present experiments are the first ones in which these bands have been excited with great intensity in an electrical discharge. Furthermore, these seem to be the first spectroscopic results, other than the continuous spectrum that was discussed earlier, that have been gotten from the air glow. In what is to follow, the origin of the β bands will be discussed and several questions of interest will be raised.

Discussion

The β bands correspond to the transition from the B level to the X electronic level of the molecule. The X level is the normal level and both the B and X levels are now thought to be $^2\Pi$ levels. Although there will be no occasion in this discussion to refer to the electronic configuration of the two levels involved the older method of identifying the two levels will not be used and they will be referred to as the $^2\Pi$ levels. It is proposed here also to use v instead of n for the vibrational quantum number in accordance with a suggestion contained in a letter[11] on band spectrum notation that was recently circulated.

The values of ω_0 for the two $^2\Pi$ levels are 1030 cm^{-1} for the upper one and 1892 cm^{-1} for the lower level. Consequently one should expect an intensity distribution among the bands that is typical of a molecule whose moments

[9] Kaplan, Phys. Rev. **34**, 165 (1929).
[10] E. P. Lewis, Phys. Rev. (1) **18**, 125 (1904); Astrophys. J. **20**, 49 (1904).
[11] O. W. Richardson, Trans. Farad. Soc. **25**, 628 (1928).

of inertia in the upper and lower states differ greatly. Barton, Jenkins and Mulliken[12] have studied the intensity distribution among the β bands that were excited in active nitrogen, and they have found that the principal features of the intensity distribution agree with the predictions of the Condon theory. They have also noted some interesting and definite discrepancies between theory and experiment and the occasion will arise later in the paper for mentioning them.

In the present experiments the most intense β bands correspond to the $v'=0$ progression. Transitions from higher $^2\Pi$ levels are either very weak or entirely absent in the discharge. Birge[13] has pointed out that the $v'=0$ progression in the β bands, as excited by active nitrogen, was very intense relative to the higher progression. In the present experiments they seem to be relatively even more intense than they are in active nitrogen. The similarity between the two methods of excitation as indicated by the above point may be interpreted as showing that the mode of excitation in the present experiments may be exactly the same as that occurring in the afterglow of nitrogen. It is not proposed to discuss here the relationship between the excitation of the β bands and the nature of the afterglow. That will be discussed elsewhere. The present experiments have suggested several questions as to the possible ways in which the β bands can be excited and it is those questions that will be briefly discussed here.

The absence of the β bands from the spectra of ordinary discharges through mixtures of nitrogen and oxygen or through nitric oxide, is of course readily accounted for by the Condon theory and is due to the large change in moment of inertia during the transition $B^2\Pi^0 \rightarrow X^2\Pi^0$. The most probable transition from the $X^2\pi^0$ level by electron impact would probably result in dissociation of the molecule. Now according to ideas advanced by R. J. Strutt, NO_2 is formed in the air afterglow by the oxidation of NO by ozone. It is possible therefore that highly vibrating nitric oxide molecules are formed by the decomposition of NO_2 in the weak discharge and it is these molecules that are excited by electron impact to yield molecules in the $B^2\Pi^0$ level. It is difficult of course to see just why this level should be favored both by this process and by the one in active nitrogen. It is also difficult to reconcile the above suggestion with the absence or weakness of other than the $v'=0$ progressions.

Before calling attention to two other possible modes of excitation another unique property of the β bands will be mentioned. Barton, Jenkins and Mulliken have called particular attention to the fact that progressions higher than $v'=4$ are absent from the β bands excited in active nitrogen. This is especially striking since in absorption bands up to $v'=5$ have been observed. The above mentioned fact may give the clue to the explanation of the excitation of these bands in both afterglows.

The energy necessary for the excitation of the $^2\Pi^0$ level from the normal state of the molecule is 5.65 volts. The energy of recombination of NO is

[12] Barton, Jenkins and Mulliken, Phys. Rev. **30**, 175 (1929).

[13] R. T. Birge, Molecular Spectra in Gases, p. 141.

now thought to be about 6.6 volts.[14] Consequently it is possible that the energy of recombination of the nitrogen and oxygen atoms is used to excite the β bands. There are several ways in which this energy transfer can be made and a detailed discussion of these possibilities will be given elsewhere. The interesting point to note here is that when it is necessary to excite a molecular level, in which the separation of the two atoms is much larger than in the initial level, there are ways, in which that can be done, that do not involve a transition from the normal to the excited level. In the present case instead of an increase in separation between the nitrogen and oxygen atoms, as would occur if the excitation were from $X^2\Pi^0 \rightarrow B^2\Pi^0$, there is a decrease in separation arising from the recombination of the two atoms. This may account for both the absence of progressions higher than $v'=4$ in the case of active nitrogen, and for the unusual intensity of the $v'=0$ progression in the present experiments as well as in active nitrogen.

One other method remains and attention has already been called to this in an earlier note by Kinsey[15] and the writer. This method is based on the hypothesis that the excitation of bands by collisions of the second kind does not necessarily obey the Condon theory and that large changes in the separation of two atoms can arise when the excitation is brought about in this way. The presence of metastable molecules in active nitrogen makes the above postulate a plausible one, although the energy of the metastable molecules is such as to make difficult the immediate explanation of the several peculiarities in the bands to which attention has been called. There are hardly enough data on the excitation of bands by collisions of the second kind to warrant any hypotheses, but the possibilities are interesting.

[14] Birge, Trans. Farad. Soc. **25**, 707 (1929).
[15] Kinsey and Kaplan, Phys. Rev. **33**, 114 (1929).

THE INFRA-RED ABSORPTION OF SOME ORGANIC LIQUIDS

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Abstract

The infra-red absorption spectra of fourteen organic compounds, including seven alcohols and seven miscellaneous compounds, have been studied in the region from 1μ to 7.5μ. The bands in the region from 1μ to 3μ have been classified as overtones or combination bands of the assumed fundamental bands for the alcohols at about 3.00μ, 3.4μ, 6.8μ, and 9.8μ. By the use of Sappenfield's work for the region from 1μ to 2μ and that of Weniger from 7.5μ to 10μ and the present work a fairly complete idea of the infra-red absorption spectra of the alcohols has been obtained. The intensity relations have been discussed briefly and it was shown that they were in general in accordance with combinations attributed to the different bands. The bands of the miscellaneous organic compounds have been classified, but all the bands have not been included as only the fundamentals at 3.4μ and 6.8μ were used. A probable reason for the similarity of the infra-red spectra of many organic compounds in the region from 1μ to 3μ has been suggested.

Introduction

AN EXPERIMENTAL study has been made of the infra-red absorption bands of fourteen organic liquids in the region from 1μ to 8μ. The materials used were methyl, ethyl, propyl, butyl, iso-propyl, iso-amyl, and iso-butyl alcohols and m-nitrotoluene, o-nitrotoluene, methyl sulphate, ethyl sulphate, nitromethane, nitrobenzene and ethyl acetoacetate. The purpose of this investigation was to see what similarities existed in the near infra-red absorption bands of some organic liquids of quite different type. Also, it was hoped that several of the more intense bands of each material could be classified as combination bands of the fundamentals.

The infra-red absorption spectra of nearly all the alcohols studied in this work have already been investigated by Weniger[1] in the region from 1μ to 14μ and by Sappenfield[2] from 1μ to 2μ. The work of Weniger gives one a good representation of the bands to 14μ, but as he used a very thin cell for the entire region many of the smaller bands were not observed. Sappenfield was able, by using cells of different thickness and spectrometer of high resolution, to detect many bands in the region from 1μ to 2μ which had not previously been observed. He classified some of the bands observed by him on the basis of the work of Gapon.[3] It was believed that a modification of his classification would be more in accordance with intensity relations. It was thought that it would be of value to extend the experimental observations under high

[1] Weniger, Phys. Rev. **31**, 388 (1910).
[2] Sappenfield, Phys. Rev. **33**, 37 (1929).
[3] Gapon, Zeit. f. Physik **44**, 600 (1927).

resolution beyond the region of 2μ and to classify the bands found by Sappenfield with those of this region.

Experimental Procedure

The apparatus and the method of measurement were essentially the same as used by the writer in a previous investigation.[4] It was found necessary to use cells of different thickness in order to observe the weaker bands. These cell thicknesses and the effective slit widths are tabulated in Table 1. The

Table I. *The cell thicknesses and the effective slit-width at the thermopile for the different parts of the region studied.*

Region	Thickness of cell	Prism used	Effective slit-width
$1.00\mu - 1.25\mu$	1.50 mm	Quartz	0.0060μ
$1.25\mu - 2.00\mu$	.7 mm		$.0075\mu$
$2.00\mu - 2.80\mu$	.4 mm		$.0150\mu$
$2.80\mu - 3.50\mu$	.01 to .001		$.0150\mu$
$5.50\mu - 7.50\mu$	.01	Rock-salt	$.155\mu$

thickness of the cells in the region from 2.80μ to 3.50μ and from 5.50μ to 7.50μ varied somewhat for each material studied. For example, in the cases of the alcohols it was necessary to have cells about 0.001 mm in order that 20 per-cent of the incident beam might be transmitted. These thin cells were made by placing a small drop of the liquid on a microscopic cover glass and then placing another cover glass over this. The cell formed in this manner was then pressed very thin and glued around the edges. An approximate value of the thickness was obtained by observing the change in the interference fringes when the cover glasses were pressed together at the center of the cell. The thicker cells were made by separating glass or rock-salt windows with lead foil or sheet lead. All the materials used in this study except two of the alcohols, which were prepared in the chemical laboratory, were obtained from the Eastman Kodak Laboratories.

Results and Discussion

The experimental results are represented in Figs. 1 to 6 and a list of the observed bands is given in Table II. The region from 2.8μ to 3.6μ was measured with the rock-salt prism in Fig. 3 and with the quartz prism in Fig. 2. Due to the great effective slit width in the region of 3μ for the rock-salt prism, it was not possible to resolve the bands at 3.00μ and 3.40μ. For the alcohols the region from 3.6μ to 5μ has been included in Fig. 3, but it does not contain any intense bands. Also, any bands of much intensity were not observed for the other materials in this region and results obtained were not included in Fig. 6. The relations found to exist between some of the bands of the alcohols are shown in Table III. The combinations given were calculated on the basis that the intense bands observed at 3.00μ, called $\nu_1{}^1$, 3.40μ, ν_1, 6.90μ, ν_2, and

[4] Plyler and Steele, Phys. Rev. **34**, 599 (1929).

TABLE II. *List of observed bands.*

Alcohols						
Methyl	Ethyl	Propyl	Butyl	Iso-propyl	Iso-amyl	Iso-butyl
2.06μ	2.03μ	2.07μ	2.07μ	2.06μ	2.05μ	2.05μ
2.27	2.23	2.16	2.18	2.28	2.27	2.10
2.46	2.42	2.27	2.30	2.42	2.39	2.25
2.56	2.54	2.43	2.44	2.54	2.56	2.38
2.92	3.01	2.62	2.60	3.00	3.01	2.50
3.02	3.39	3.01	3.00	3.38	3.42	2.99
3.29	4.31	3.43	3.43	4.22	4.61	3.41
3.42	5.00	4.55	3.22	4.44	5.16	4.52
4.22	5.75	4.91	4.67	5.72	5.69	4.78
4.70	6.11	5.18	5.07	5.98	5.92	5.18
5.42	6.62	5.81	5.93	6.10	6.80	5.86
5.84	6.89	6.06	6.13	6.71	6.96	6.86
6.14	7.04	6.67	6.83	6.91	7.14	7.00
6.73	7.40	6.81	6.95	7.24	7.79	7.88
6.99	7.81	7.91	7.98			
7.38						
7.82						

M-nitro-toluene	O-nitro-toluene	Methyl sulphate	Nitro-methane	Ethyl sulphate	Nitro-benzene	Ethyl acetoacetate
1.15μ	1.15μ	1.15μ	1.12μ	1.17μ	1.13μ	1.17μ
1.39	1.40	1.38	1.37	1.39	1.29	1.40
1.68	1.67	1.67	1.68	1.71	1.42	1.65
1.98	2.00	1.86	1.82	1.91	1.63	1.92
2.04	2.30	1.97	1.92	2.05	1.80	1.99
2.31	2.41	2.06	2.26	2.30	1.90	2.29
2.47	2.54	2.24	2.41	2.43	2.15	2.40
2.55	3.28	2.37	2.59	3.37	2.44	2.62
3.28	3.39	2.60	3.29	7.20	3.26	3.39
3.42	6.68	3.40	3.41		3.43	5.82
6.57	7.46	7.05	6.37		6.56	7.10
7.40		7.20	7.13		7.36	

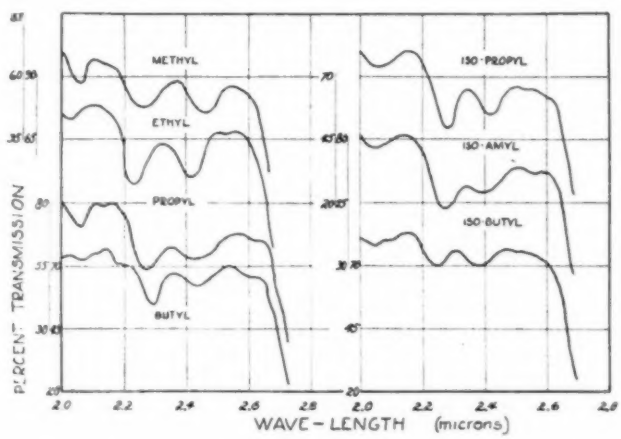

Fig. 1. The percent transmission of methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, iso-propyl alcohol, iso-amyl alcohol and iso-butyl alcohol in the region from 2μ to 2.7μ, the cell thickness being 0.4 mm.

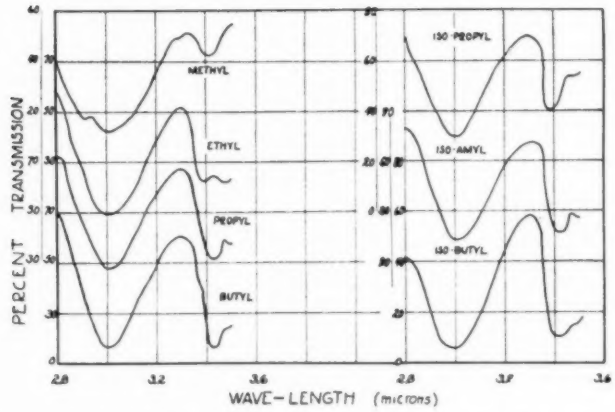

Fig. 2. The percent transmission of methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, iso-propyl alcohol, iso-amyl alcohol and iso-butyl alcohol in the region from 2.8μ to 3.5μ, the cell thickness being from 0.01 to 0.001 mm.

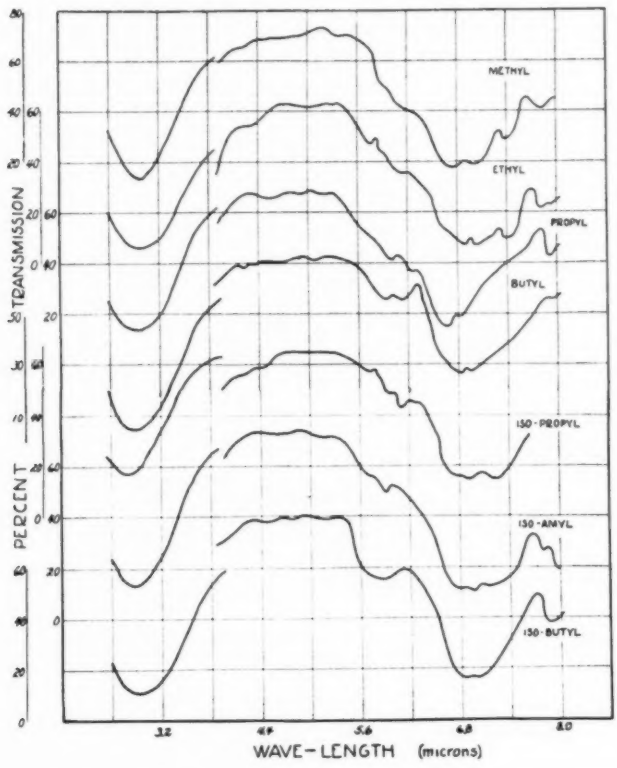

Fig. 3. The percent transmission of methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, iso-propyl alcohol, iso-amyl alcohol and iso-butyl alcohol in the region from 2.8μ to 8μ, the cell thickness being from 0.01 to 0.001 mm.

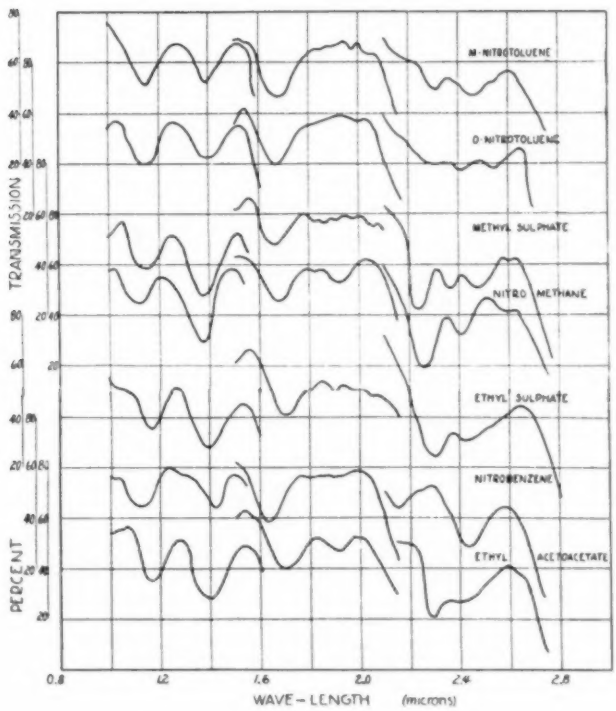

Fig. 4. The percent transmission of m-nitrotoluene, o-nitrotoluene, methyl sulphate, nitromethane, ethyl sulphate, nitrobenzene, and ethyl acetoacetate in the region from 1μ to 2.8μ, the cell thickness being 15 mm from 1μ to 1.25μ, 0.7 mm from 1.25μ to 8.2μ, and 0.4 mm from 2.00μ to 2.8μ.

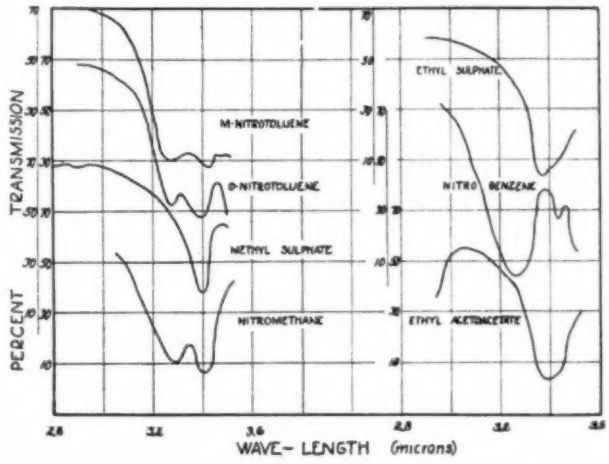

Fig. 5. The percent transmission of m-nitrotoluene, o-nitrotoluene, methyl sulphate, nitromethane, ethyl sulphate, nitrobenzene, and ethyl acetoacetate in the region from 2.8μ to 3.5μ, the cell thickness being about 0.01 mm.

9.8μ, ν_3, were the fundamental bands. The combinations which the bands are attributed to are made up of only two or three of the fundamentals or their overtones as it is probable that more intense bands will be produced by simple

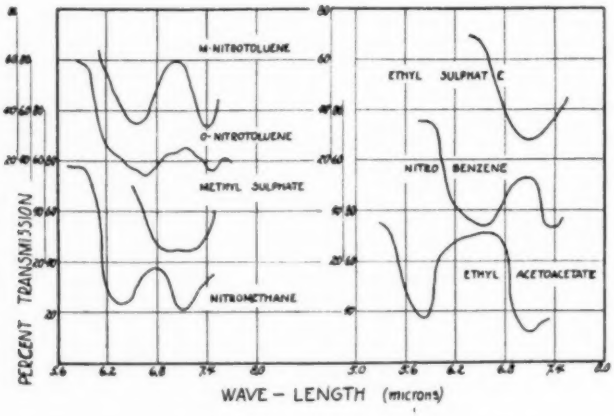

Fig. 6. The percent transmission of m-nitrotoluene, o-nitrotoluene, methyl sulphate, nitromethane, ethyl sulphate, nitrobenzene, and ethyl acetoacetate in the region from 5.5μ to 7.5μ, the cell thickness being about 0.01 mm.

combinations. All the observed bands have not been assigned to combinations as it was found necessary to include up to the fifth or sixth overtone as one of the terms to obtain good agreement between the observed and calculated results. It was believed that the bands at about 1.94μ and 2.60μ

TABLE III. *Calculated and observed bands in the alcohols.*

	Propyl alcohol obs.	Propyl alcohol calc.	Butyl alcohol obs.	Butyl alcohol calc.	Iso-butyl alcohol obs.	Iso-butyl alcohol calc.
$4\nu_1$	0.923μ	0.923μ	0.929μ	0.929μ	0.918μ	0.918μ
$3\nu_1^1$	1.028	1.028	1.032	1.032	1.025	1.025
$\nu_1+2\nu_1^1$		1.06		1.06		1.06
$\nu_1^1+2\nu_1$		1.11		1.10		1.11
$3\nu_1$	1.198	1.198	1.203	1.203	1.196	1.196
$\nu_1^1+\nu_1+\nu_3$		1.37	1.43	1.37	1.41	1.37
$2\nu_1$	1.53	1.53	1.53	1.53	1.53	1.53
$\nu_1^1+\nu_1$	1.58	1.60	1.59	1.60	1.58	1.60
$\nu_1^1+\nu_2+\nu_3$	1.71	1.71	1.72	1.72	1.71	1.72
$2\nu_1$	1.71	1.76	1.72	1.75	1.71	1.77
$\nu_1+\nu_2+\nu_3$		1.84		1.82		1.83
$\nu_1^1+\nu_2$	2.07	2.08	2.07	2.09	2.10	2.09
$\nu_1+\nu_3$	2.27	2.27	2.30	2.29	2.25	2.28
$\nu_1^1+\nu_3$	2.27	2.29	2.30	2.29	2.25	2.29
ν_1^1	3.01	3.05	3.00	3.03	2.99	3.03
ν_1	3.43	3.44	3.43	3.40	3.41	3.47
ν_2	6.73	6.73	6.83	6.85	6.86	6.90
ν_3	9.60	9.60	9.75	9.75	9.75	9.75

which were omitted, were due to a combination including a fundamental beyond 12μ which had not been observed rather than to a combination of the known fundamentals. Fundamental bands have been observed for several

organic compounds in this region and it is probable that they exist for these materials, and if they were known, probably a more complete classification could be made.

By a study of the experimental results it is seen that there is considerable overlapping of the bands in the near infra-red region. Unless high resolution is used the less intense maxima are not observed. Also often a weak band occurs near an intense one and changes the shape of the more intense absorption curve, but does not cause the absorption curve to change sufficiently for it to be detected. This effect is especially noticeable in the alcohols in the region from 1.4μ to 1.6μ.

Sappenfield[2] has used the suggestion of Ellis[5] that the organic liquids may be arranged as a series of overtones of the 3.4μ band and thus four of the bands are classified. This classification appears probable and the writer has included it in the present arrangement. The band at 0.92μ was classified as $4\nu_1$ and the band at 1.20μ as $3\nu_1$, and $2\nu_1$ and ν_1 were calculated from these bands. However, as a small error in $4\nu_1$ and $3\nu_1$ would cause a large error in ν_1 it was thought that the observed value of ν_1 was more accurate and it was used in the calculation of the combination bands. In like manner ν_1^1 was checked by using the bands at 1.02μ as $3\nu_1^1$ and 1.53μ as $2\nu_1^1$, but in combination bands the observed value of ν_1^1 was used. It should be noted in some cases there is a considerabel difference between the calculated and observed bands in the case of $2\nu_1$ at about 1.75μ. This difference is probably brought about by the fact that the combination $\nu_1^1+\nu_2+\nu_3$ also gives rise to a band at near the same wave-length. In the case of tertiary butyl alcohol and secondary butyl alcohol both maxima were found.

By an examination of the results obtained in this work and those obtained by Weniger[1] the intensities of the assumed fundmentals are in the order ν_3, ν_1^1, ν_2, and ν_1. Of the combination bands obtained by adding two fundamental bands $\nu_1^1+\nu_3$ should probably be the most intense and $\nu_1+\nu_2$ the least intense. However, these two bands fall in the same region of the spectrum and were not separated. The intensity of $\nu_1^1+\nu_1$ in the region of 1.60μ is somewhat less than the intensity of $\nu_1^1+\nu_2$ at 2.09μ and the intensity of $\nu_1^1+\nu_1+\nu_3$ is less than that of $\nu_1^1+\nu_1$. The decrease in intensity of the successive overtones of ν_1^1 and ν_1 is large. Due to the considerable overlapping in the bands, it is not possible to made a careful comparison of the intensities of the different combinations, but in the bands where the intensities could be checked the combinations given in Table III were upheld.

In Table IV the assumed fundamentals ν_1 at 3.40μ and ν_2 at 6.80μ and combination bands of M nitrotoluene, methyl sulphate, nitromethane are given. Only slight differences occur for the other materials studied and they have not been included. Since only two fundamentals are known, several of the bands in the near infra-red could not be attributed to simple combinations. They have been omitted for they are possibly due to combinations of ν_1 and ν_2 with bands in the region of 10μ to 12μ and 15μ to 18μ. In these

[5] Ellis, Phys. Rev. **31**, 916 (1928).

regions bands have been shown to exist for several of methyl and ethyl compounds by different observers.[6]

While it must be recognized that the infra-red absorption spectra of each substance are different even though they may be only slightly different chemically, yet the great similiarity in the absorption spectra of quite different organic compounds in the region from 1μ to 3μ is readily observed. This similarity in the near infra-red region is probably due to the fact that many

TABLE IV. *Combination bands in nitrotoluene, methyl sulphate and nitrobenzene.*

	M-nitro-toluene obs.	calc.	Methyl sulphate obs.	calc.	Nitro-benzene obs.	calc.
$3\nu_1$	1.15μ	1.15μ*	1.15μ	1.15μ*	1.13μ	1.13μ*
$2\nu_1+\nu_2$	1.39	1.35	1.38	1.35	1.29	1.32
$2\nu_1$	1.68	1.68*	1.67	1.67*	1.63	1.63*
$\nu_1+\nu_2$	2.21	2.21	2.24	2.29	2.15	2.21
ν_1	3.28	3.27	3.40	3.24	3.26	3.13
$2\nu_2$	3.42		3.40		3.43	
ν_2	6.80	6.80*	7.05	7.05*	6.90	6.90*

* Experimental values used as calculated values.

organic compounds have fundamentals at about 3.3μ and 6.8μ, and in several cases also, fundamental bands are in the region from 8μ to 12μ and from 12μ to 18μ. By the combinations of these bands the near infra-red spectra are somewhat similar in appearance, but in the region from 8μ to longer wavelengths a considerable difference is found in the spectra of similar organic compounds. An examination of the results of Coblentz[6] shows this for a large number of organic compounds.

[6] Coblentz, Investigations of Infra Red Spectra, Part 1–2, Carnegie Institution of Washington, (1905).

MEASUREMENT OF THE DIELECTRIC CONSTANT AND INDEX OF REFRACTION OF WATER AND AQUEOUS SOLUTIONS OF KCl AT HIGH FREQUENCIES

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Abstract

Dielectric constant of distilled water.—The dielectric constant of distilled water was measured with a vacuum tube source of voltage throughout a range of periods extending from about $T=1.31\times10^{-8}$ second to $T=8.49\times10^{-8}$ second corresponding to vacuum wave-lengths of 3.918 meters to 25.47 meters. The value obtained for the dielectric constant is $\epsilon=78.57$ at 25°C and is independent of the period within the above range of periods.

Temperature coefficient of dielectric constant for distilled water.—The values of the dielectric constant ϵ obtained for various temperatures t between 10°C and 60°C satisfy the empirical equation

$$\epsilon_t=78.57[1-0.00461(t-25)+0.0000155(t-25)^2\cdots].$$

Between 4°C and 10°C the applicability of this equation is somewhat uncertain.

Dielectric constant of conducting solutions.—With distilled water, tap water, and aqueous KCl solutions of conductivity ranging from 0.97×10^7 e.s.u. to 178×10^7 e.s.u., and separating the conduction effects from the dielectric effects, we found the dielectric constant only slightly dependent on the ionic concentration of the solution and nearly the same as that of pure water. The errors of measurement are of the order of 0.1 percent for low conductivities but, because of attenuation, become of the order of 1 percent at the high concentrations of the salt.

Method.—The method employed consists in the measurement of standing electric waves between a pipe and a wire concentrically located within the pipe. The liquid is the dielectric between the wire and the pipe. The frequencies employed were accurately measured by a piezo crystal standardizing a zero beat method, and the half wave-length within the dielectric were obtained by moving a piston in the liquid and observing reactions on the source.

A theoretical discussion of the method is given.

Introduction

SOON after the discovery of piezoelectric oscillators and their adaptation to the production of constant frequencies of oscillations[1] we began an investigation of waves on wires. The frequencies of an electric oscillator were determined by comparison with the piezoelectric standard and the lengths of the resulting standing waves on two parallel wires were measured. In this way

[1] G. W. Pierce, "Piezoelectric Crystal Resonators and Crystal Oscillators Applied to the Precision Calibration of Wavemeters," Proc. Am. Acad. of Arts and Sciences **59**, No. 4 (1923). "Piezoelectric Crystal Oscillators Applied to the Precision Measurement of the Velocity of Sound etc." Ibid. **60**, No. 5 (1925).

an absolute determination of the ratio of the electro-magnetic to the electrostatic unit of electric quantity was attempted. After about a year of work on this problem it became apparent that the influence of surrounding objects led to errors and uncertainties which could not be sufficiently reduced with the parallel wire system.

To avoid this stray-field trouble it occurred to us to confine the field to the space between a central wire and a surrounding tube. This apparatus we have now had in operation for several years. The investigation with air or vacuum as the dielectric is not yet good enough for publication since on account of certain small mechanical inequalities of the pipe-system the precision desired has not been attained. We have, however, obtained accuracies better than one-tenth of one percent, and as a by-product to the primary research on the ratio of the units we have employed a similar apparatus in the present investigation.

Details of the Concentric Pipe System

The present method of determining the index of refraction of poorly conducting liquids resembles the older well-known scheme of measuring the index by comparing the length of the standing waves on Lecher wires immersed in the liquid with the length of the corresponding air waves. The method is, however, here refined by replacing the wires of the Lecher system by a brass pipe having a copper wire centrally within it along the axis of the pipe, with the solution in the pipe. The pipe and wire are excited by a vacuum tube oscillator at frequencies accurately known by their harmonic relationship with a piezoelectric quartz standard. A movable brass plunger making spring contacts with the pipe and wire and carrying a calibrated rod of the same material above it permits accurate settings at the positions of maximum reaction, which are half a wave-length apart. A sensitive galvanometer, recording changes in the plate current of the oscillator exciting the pipe and wire, indicates the half wave positions as the plunger moves along the pipe. From the known frequencies and the wave-length in the dielectric the velocity of the electric waves in the dielectric is computed.

As a device for producing standing electric waves the system of pipe, wire, and plunger has the outstanding advantage of confining the electric field to the medium between the pipe and wire. Suppose, for example, a set of parallel wires is immersed in a water tank. If the tank is small, an appreciable part of the electric field associated with the charges on the wires may be quite outside the water; difficulties also arise from reflections at the boundaries of the water; and an increase in size of the tank only reduces and does not eliminate these disturbances. For the longer waves in the present experiments the tank would need to be enormous. In the case of the pipe and wire system, on the other hand, the electric currents are confined to the inner surface of the pipe and the outer surface of the wire, so that the electric field has radial symmetry and is completely within the dielectric.

Fig. 1 shows in detail the experimental arrangements adopted. The brass pipe, 3.7 meters long and having an inside diameter of 4.1 cm and a wall-

thickness of 0.32 cm, was mounted vertically against a wall between two neighboring floors of the Cruft laboratory. A hard-drawn copper wire 0.163 cm in diameter was centrally fixed in the pipe held at the lower end by a canvas bakelite cap, and at the upper end by a bakelite strip. In order to make a watertight joint at the lower end, the bakelite cap was screwed to the end of the pipe hard against a thin cardboard gasket which had been boiled in paraffin. The pipe was filled from the top and emptied through a small hole (normally closed with a bakelite plug) in the bakelite cap.

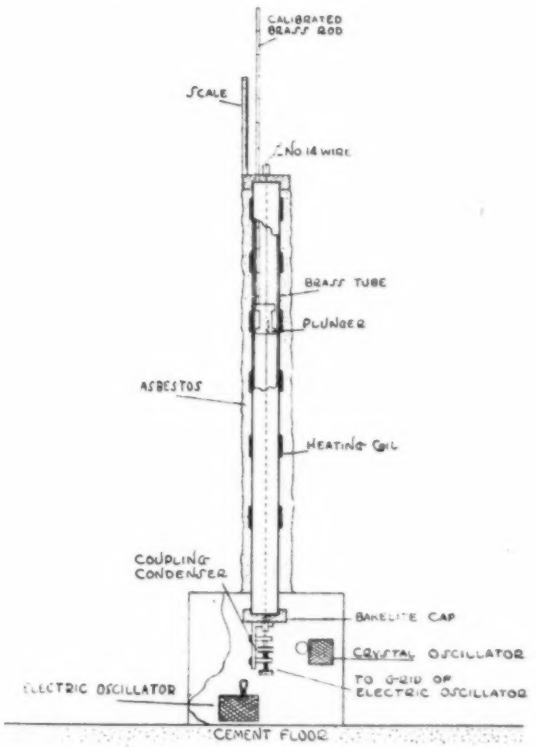

Fig. 1. Arrangement of apparatus.

Two electric oscillators were used to cover the range from 4 to 25 meters vacuum wave-length: one, an oscillator designed particularly for high frequencies, covered the range from 4 to 5 meters; the other, an ordinary Hartley circuit oscillator with parallel plate supply, was used from 5 to 25 meters. These two oscillators and the piezo-electric oscillator, employing a quartz crystal mounted in vacuum, were placed in a sheet iron box at the lower end of the pipe. The pipe protruded below the cover of this box about 10 cm, and made good contact with the cover by means of a bronze flange clamped about the pipe and bolted to the cover. Shielded cables included all electrical connections from the observing position at the top of the pipe to the various oscillators in the box below. The electric oscillator was coupled to the lower end

of the pipe-wire by a single lead through a small condenser, which was variable in order to permit equal coupling at all frequencies. The adjustment to zero beat between the electric oscillator and a harmonic of the crystal oscillator was accomplished by varying a condenser of the electric oscillator for course adjustment; and finally, for fine adjustment, a resistance in the plate circuit of the electric oscillator was varied.

The reflection of waves at the input end occurs principally at the lower surface of the water column, that is, the upper surface of the bakelite cap, due to the large discontinuity in dielectric constants here. The waves are reflected at the other end by a solid brass plunger making spring contact at its lower face with the pipe and wire, and moved by a brass rod 0.6 cm in diameter firmly fixed to the plunger, and upon which are cut marks 50 cm apart. As the piston is moved the current in the plate circuit of the driving oscillator remains constant until the piston is in the neighborhood of a potential node, and then shows a marked change in value as the node is passed due to the reaction of the waves on the oscillator. These nodal positions can be determined with an accuracy of about 0.1 mm with water as dielectric.

Standard of Frequency

The length of a wave in vacuum was computed from the velocity of light and the frequency of the particular harmonic employed. The piezoelectric crystal used as a standard vibrates at a temperature of 25°C with a frequency $f_0 = 5.886 \times 10^6$ cycles per second. In Table I are given the periods and half wave-lengths in vacuum corresponding to the employed harmonics of this crystal from the second to the thirteenth inclusive. Harmonic numbers are tabulated in the first column under p. The fundamental frequency is characterized by $p=1$. The periods (T) are in seconds, and the vacuum half wave-lengths ($\lambda_0/2$) are in centimeters.

Table I. *Periods and vacuum half wave-lengths for different harmonics of the crystal standard.*

p	$T\times10^8$	$\lambda_0/2$	p	$T\times10^8$	$\lambda_0/2$	p	$T\times10^8$	$\lambda_0/2$
2	8.49	1273.5	6	2.83	424.5	10	1.70	254.7
3	5.66	849.0	7	2.42	363.9	11	1.54	231.5
4	4.25	636.8	8	2.12	318.4	12	1.41	212.3
5	3.40	509.4	9	1.89	283.0	13	1.31	195.9

Theory

The velocity of propagation of electric waves along coaxial tubes is the ratio of the angular velocity of the exciting current to the retardation angle per unit length of the tubes. That is, if β is retardation angle per unit length of tube, $\omega/2\pi$ the frequency of electric oscillator and v the velocity of electric waves of frequency, $\omega/2\pi$, then

$$v=\omega/\beta. \tag{1}$$

The retardation angle β depends rather simply upon two coefficients of the line: one involving the series resistance and inductance per loop unit length

of the line, and the other involving the capacity and leakage conductance per loop unit.

Let r, l, c, g be respectively resistance, inductance, capacity, and leakage conductance per loop unit of length for the pipe and wire; μ, ϵ be respectively the permeability and dielectric constant of the medium between the pipe and the wire.

$$\eta = r/l\omega$$

$$s = g/c\omega$$

$$f(h) = +\left(\frac{(1+h^2)^{1/2}+1}{2}\right)^{1/2}$$

$$g(h) = +\left(\frac{(1+h^2)^{1/2}-1}{2}\right)^{1/2}. \qquad \text{See Footnote 2.}$$

It will be later shown that in these experiments $\eta S < 1$ so that, since $\mu = 1$, the retardation angle β is given by the leaky-line equation:

$$\beta = \frac{\omega}{c'}\epsilon^{1/2}(1-\eta s)^{1/2} f(h) \qquad (2)$$

where

$$h = \frac{\eta + s}{1-\eta s}$$

c' = ratio of the units.

Since from Maxwell's theory the velocity of electromagnetic waves in vacuum is numerically equal to the ratio of the units (a fact that we have checked experimentally to better than one part in 3000), the index of refraction, corresponding to Eq. (2), is, in view of (1),

$$N = \epsilon^{1/2}(1-\eta s)^{1/2} f(h). \qquad (3)$$

The index N is directly measured in these experiments as the ratio of the wave-length in vacuum to the wave-length in the water.

Eq. (3) then gives a means of calculating the dielectric constant ϵ from values of N and the line coefficients η and s. It will be noted that s and h both involve ϵ through c, the capacity per loop unit of length.

With the object of still further simplifying (3) let us examine the magnitudes of η and s for the actual line. By substitution of the values of g and c in terms of the inner radius of the pipe and the outer radius of the wire it may be shown that

$$s = \frac{2\gamma T}{\epsilon}$$

[2] Cf. G. W. Pierce, "A Table and Method of Computation etc," Proc. Am. Acad. 57, No. 7 (1922), where these functions, which occur frequently in electromagnetic theory, have been computed and tabulated for values of h between 0 and 250.

where γ is the specific conductivity of the medium between pipe and wire in e.s.u. and T is the period in seconds corresponding to angular velocity ω. Since it is known before hand that ϵ is sensibly independent of frequency, s will be a maximum where the product $T\gamma$ is largest. This occurred in our experiments for waves of period 2×10^{-8} second and for a conductivity of 178×10^{7} e.s.u. Since ϵ is approximately 78.5 for water we find

$$s\leqq 0.96.$$

The exact value of η for a particular frequency cannot be calculated unless the value of the resistance per loop unit of pipe and wire is known. A value of η sufficiently near the actual value to discuss negligibilities in Eq. (3) may, however, be obtained by assuming that the resistance of the pipe is negligible in comparison with the resistance of the wire.

With this approximation it may be shown, by putting in numerical values, that for the conditions in the present investigation

$$\eta\leqq 0.0035$$

and

$$\eta s\leqq 0.0034.$$

These results permit considerable simplification in Eq. (3). In the first place, it is evident from inspection of tabulated values of the function $f(h)$ that for all values of h for which $f(h)$ contributes to Eq. (3) a multiplier different from unity the expression for h may be reduced to

$$h=s=2\gamma T/\epsilon$$

without affecting the accuracy by one part in a thousand. Finally, the maximum error which would be produced by neglecting ηs in comparison with unity under the radical of Eq. (3) will be approximately $\eta s/2$ or about one part in six hundred. But so large an error would occur only for the highest conductivities and lowest frequencies, for which, because of high damping, the accuracy of the experimental determinations is reduced to approximately one part in two hundred; so that the final accuracy of computed observations will not be appreciably affected if we write for all cases in these experiments,

$$N=\epsilon^{1/2}f(h) \tag{4}$$

where

$$h=2\gamma T/\epsilon$$

Eq. (4) is the theoretical expression for the index of refraction of water and aqueous solutions for the particular frequencies, conductivities, and physical dimensions employed in the work herein described. γ and ϵ are respectively the conductivity in e.s.u. and dielectric constant in e.s.u. of the water or the solution, and T is the period of the electric waves.

Measurements of the Dielectric Constant of Distilled Water in the Range of Periods 1.31×10^{-8} to 8.49×10^{-8} Second

Table II gives a series of results obtained for distilled water at approximately 25°C. The first column contains the number of the harmonic of the

standard crystal oscillator with which the electric oscillator was held at zero beat-frequency. From Table I the corresponding values of the half vacuum wave-length $\lambda_0/2$ are taken and are tabulated in column II. Column III contains the temperature, column IV the measured value of half wave-length in the water at temperature t, conductivity γ; column V the half wave-length reduced to 25°C by use of the coefficient obtained below; column VI the value of index of refraction N at 25°C. The next to the last column contains approximate values of $2\gamma T/\epsilon$, in which only a rough value of ϵ is needed. For $h=0.0212$, in the top line of the table, the value of $f(h)$ as defined above is 1.00005 and can be replaced by unity. For larger values of p $2\gamma T/\epsilon$ is still nearer unity; so throughout the table the correction for γ is negligible, making ϵ in the last column of this table the same as the square of the sixth column.

TABLE II. *Distilled water, of conductivity* $\gamma=0.97\times10^7$ *e.s.u.*

p	$\lambda_0/2$	t	$\lambda/2(t, \gamma)$	$\lambda/2(25, \gamma)$	$N(25, \gamma)$	$2\gamma T/\epsilon$	ϵ_{25}
2	1273.5	25.5	143.95	143.79	8.856	.0212	78.43
3	849.0	"	95.93	95.82	8.860	.0141	78.50
4	636.8	"	71.89	71.81	8.867	.0106	78.62
5	509.4	"	57.50	57.44	8.868	.0085	78.64
6	424.5	"	47.94	47.89	8.864	—	78.57
7	363.9	"	41.08	41.03	8.868	—	78.64
8	318.4	25.4	35.96	35.92	8.864	—	78.57
9	283.0	"	31.97	31.93	8.864	—	78.57
10	254.7	"	28.77	28.73	8.866	—	78.61
11	231.5	25.7	26.16	26.13	8.861	—	78.52
12	212.3	"	23.97	23.95	8.862	—	78.54
13	195.9	"	22.11	22.09	8.870	—	78.68
							Mean = 78.57
							Mean departure = ± 0.05

The mean value of ϵ at 25°C is

$$\epsilon_{25}=78.57\pm0.05$$

for distilled water.

MEASUREMENTS OF THE TEMPERATURE COEFFICIENT OF THE DIELECTRIC CONSTANT OF DISTILLED WATER

Water temperatures from 3° to 60°C were obtained by filling the pipe with water just above the freezing point, allowing the pipe to warm slowly to room temperature, taking velocity measurements as different temperatures were reached. For higher temperatures heat was applied to the pipe by passing current through several coils of resistance wire wound around it, as shown in Fig. 1. The pipe was covered with asbestos packing to prevent rapid temperature changes. This precaution, in addition to the stirring produced by moving the plunger, insured a practically uniform temperature throughout the water in the pipe except near the ends, which regions could not be included in the temperature coefficient measurements. The temperature of the water before and after the wave-length measurement was read by a mercury thermometer provided with a cylinder for collecting water and holding it

around the thermometer bulb as the thermometer was raised to read. This method allowed temperatures to be determined within about 0.2°C once the operator developed sufficient speed in pulling up the thermometer and taking readings.

The values obtained for ϵ_t were found to satisfy the empirical equation

$$\epsilon_t = 78.57[1 - 0.00461(t-25) + 0.0000155(t-25)^2 \cdots]$$

for temperatures between 10° and 60°C, as seen by reference to Fig. 2 where the curve is the curve of the equation and the points are observed values of ϵ_t. Three different vacuum wave-lengths λ_0 were employed, and the points for the three different values of λ_0 all fall near the curve in the specified range of temperatures 10° to 60°C.

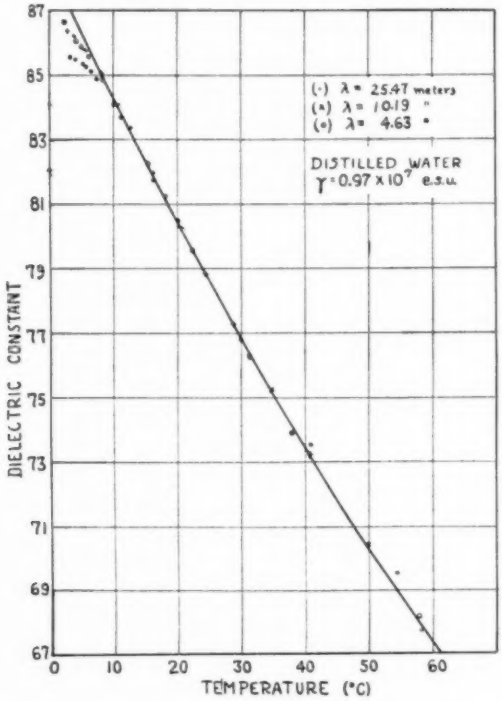

Fig. 2. Locus of empirical equation for the dielectric constant of distilled water as a function of temperature. Observed values for three wave-lengths are included.

For temperatures between 5° and 10°C there is a significant departure from the curve of the equation and the longer wave-lengths seem to give values of ϵ_t departing farther from the curve. These anomalies appear at values of temperature for which the water has anomalous behavior as to density.

Index of Refraction and Dielectric Constant of Tap Water and of Aqueous KCl Solutions

Tables III, IV, and V give measured values $\lambda/2(t, \gamma)$ of the half wave-length in tap water of conductivity $\gamma = 11.9 \times 10^7$ e.s.u., aqueous KCl-solu-

tion of $\gamma = 47 \times 10^7$ e.s.u. and KCl-solution of $\gamma = 178 \times 10^7$ e.s.u., all measured for the various values of $\lambda_0/2$ indicated in the second column of each table. Using the temperature coefficient formula of the preceding section and ex-

TABLE III. *Tap water, of conductivity* $\gamma = 11.9 \times 10^7$ *e.s.u.*

p	$\lambda_0/2$	t	$\lambda/2(t, \gamma)$	$\lambda/2(25, \gamma)$	$N(25, \gamma)$	$2\gamma T/\epsilon$	ϵ_{25}
2	1273.5	26.6	142.66	142.16	8.958	0.257	78.95
3	849.0	"	96.14	95.80	8.862	.171	77.91
4	636.8	"	71.73	71.48	8.909	.129	79.04
5	509.4	"	57.36	57.16	8.912	.103	79.26
6	424.5	"	47.93	47.76	8.899	.086	78.85
7	363.9	"	41.12	40.98	8.878	.074	78.66
8	318.4	"	36.01	35.88	8.874	.064	78.55
9	283.0	"	31.98	31.87	8.881	.057	78.71
10	254.7	"	28.83	28.73	8.866	.051	78.45
11	231.5	26.5	26.15	26.06	8.885	.047	78.78
12	212.3	"	23.97	23.89	8.885	.043	78.78
13	195.9	"	22.15	22.08	8.873	.040	78.57
							Mean = 78.71
							Mean departure = ± 0.23

TABLE IV. *KCl solution, about 1/270 normal, of conductivity* $\gamma = 47 \times 10^7$ *e.s.u.*

p	$\lambda_0/2$	t	$\lambda/2(t, \gamma)$	$\lambda/2(25, \gamma)$	$N(25, \gamma)$	$2\gamma T/\epsilon$	ϵ_{25}
2	1273.5	26.6	—	—	—	—	—
3	849.0	"	90.63	90.31	9.401	0.687	79.92
4	636.8	"	68.77	68.53	9.292	.516	81.21
5	509.4	"	55.82	55.62	9.159	.413	80.62
6	424.5	26.8	47.16	46.97	9.038	.344	79.44
7	363.9	"	40.69	40.53	8.977	.294	78.84
8	318.4	26.7	35.79	35.66	8.928	.258	78.45
9	283.0	26.9	31.86	31.73	8.919	.230	78.45
10	254.7	27.1	28.80	28.67	8.884	.207	78.45
11	231.5	27.3	26.15	26.02	8.898	.187	78.15
12	212.3	27.4	23.96	23.83	8.906	.171	78.68
13	195.9	27.3	22.18	22.07	8.877	.159	78.32
							Mean = 79.24
							Mean departure = ± 0.88

TABLE V. *KCl solution, about 1/70 normal, of conductivity* $\gamma = 178 \times 10^7$ *e.s.u.*

p	$\lambda_0/2$	t	$\lambda/2(t, \gamma)$	$\lambda/2(25, \gamma)$	$N(25, \gamma)$	$2\gamma T/\epsilon$	ϵ_{25}
8	318.4	25.6	32.87	32.83	9.698	0.960	78.73
9	283.0	"	29.64	29.60	9.560	.856	78.94
10	254.7	"	27.06	27.02	9.427	.770	78.57
11	231.5	"	24.66	24.63	9.401	.697	79.56
12	212.3	"	22.78	22.75	9.331	.639	79.56
13	195.9	"	21.26	21.23	9.228	.593	78.70
							Mean = 79.01
							Mean departure = ± 0.33

tracting the square root we have the approximate relation $\Delta\lambda/\lambda = -0.0023\Delta$ for change of wave-length with change of temperature, and have reduced the measured values of $\lambda/2$ to the values at 25°C recorded in the column marked

"$\lambda/2(25, \gamma)$." Dividing this into $\lambda_0/2$ we obtained $N(25, \gamma)$. Then employing the formula $N = \epsilon^{1/2} f(h)$, which has above been shown to be a correct approximation within the limits of period and conductivity here occurring, we have calculated the values of ϵ given in the last columns of the tables. In examining these results it should be borne in mind that large conductivities and long waves have a higher attenuation and introduce greater difficulties of measurement, which accounts for the fact that departures of readings from their average values are greater with the larger conductivities and with the longer vacuum wave-lengths. (In fact with the solution of Table V the two nodal points necessary for determining the $\lambda/2$ in the solution could not be obtained for $\lambda_0/2$ greater than 318.4 cm). Taking into account these larger sources of error we see that the addition of salts in sufficient quantity to increase the conductivity from 0.97×10^7 to 178×10^7 increases the index of refraction, in

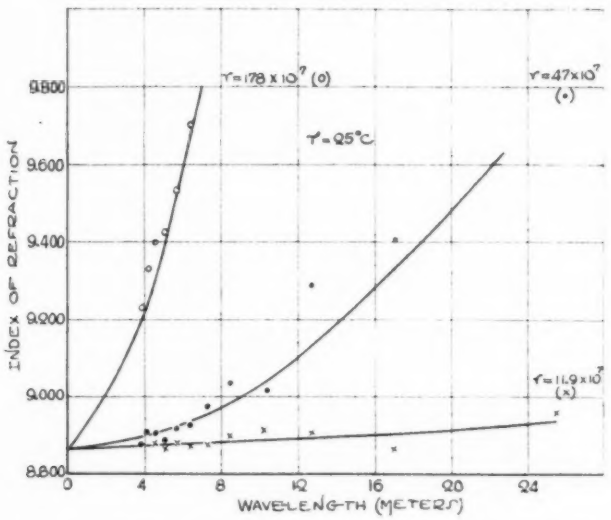

Fig. 3. Theoretical variation of the index of refraction of tap water ($\gamma = 11.9 \times 10^7$) and aqueous solutions of KCl ($\gamma = 47 \times 10^7$ and $\gamma = 178 \times 10^7$) with wave-length, assuming the true dielectric constant ϵ independent of the conductivity. Observed points are included.

a manner dependent on γ and λ_0, but when the effects of conductivity are eliminated so as to give the true dielectric constant ϵ, the value obtained for ϵ differs from ϵ of distilled water by less than 1 percent. It is not yet known whether this small difference is due to errors introduced by the high attenuation at the higher conductivities; errors which do not arise when water or low-conductivity solutions are employed.

Fig. 3 exhibits graphically as a function of wave-length the values of the index of refraction N taken from the sixth column of Tables III, IV, and V. The smooth curves are the loci of Eq. (4) for the conductivities listed above the tables; and are plotted assuming that ϵ is independent of γ and of the same value as for distilled water. The fact that the observed values lie near these theoretical curves is evidence for the validity of the assumption that ϵ is sensibly independent of γ for the conductivities here employed.

MEASUREMENTS OF THE DIELECTRIC CONSTANTS OF CONDUCTING MEDIA

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Abstract

It is possible to build small, rigid circuits which have natural periods determined by the medium in which they are immersed. If $T\gamma$, the product of the natural period of the circuit and the conductivity of the medium, is sufficiently small, this period is proportional to the square root of the dielectric constant of the latter. On the basis of this fact measurements have been made of the dielectric constant of water from 0° to 100°C to an accuracy of 0.2 percent or better and covering a range of frequency from $T = 1.4 \cdot 10^{-8}$ to $81 \cdot 10^{-8}$. If $T\gamma$ is not sufficiently small, the period is affected by the conductivity of the medium in a complicated way and cannot be used to obtain the dielectric constant. With the smallest circuits used measurements of the dielectric constants of liquids having conductivities as high as 100 times that of water can be made.

A FEW months ago I became interested in the question of the measurement of the dielectric constants of solutions of certain biological substances, chiefly various proteins which can be prepared in very pure form. Such measurements have an interest in view of existing speculations.[1]

The materials in question are for the most part best available in aqueous solution, where they behave like ampholytes containing very weak acid and basic groups.[2] Under the most favourable conditions concentrated solutions (20–30%) can be obtained having conductivities as low as ten times that of distilled water. They are, moreover, laborious to prepare in more than small quantities. Any method suitable for the study must therefore (1) be appropriate for use with material having a conductivity approaching that of a dilute salt solution and (2) be applicable to small amounts of the substance to be investigated.

The method described in this paper seems to be the simplest and most accurate one which meets these requirements and ought to be generally useful. It has, moreover, some interest in connection with the behaviour of circuits at high frequencies. The following other methods may be mentioned briefly.

The well-known bridge method of balancing the resistance and capacity of a cell containing the unknown liquid for an alternating e.m.f. of fixed frequency has been developed in great detail by Nernst.[3] It requires only

[1] Debye, Polar Molecules, Chemical Catalogue Co., New York, 1929.

[2] E. J. Cohn, Physiological Reviews **5**, 350 (1925).

[3] See Nernst, Zeits. f. Phys. Chemie **14**, 622 (1894). The method has been used by B. B. Turner, Zeits. f. Phys. Chemie **35**, 428 (1900), to measure the dielectric constant of water and several other liquids. It has also been used by Ratz, Zeits. f. Phys. Chemie **19**, 94 (1896) and

small amounts of material but it is not suitable for frequencies above about 10^6 sec^{-1}, such as are necessary for measurements on liquids having conductivities much greater than that of distilled water.

Another well-known method makes use of standing waves produced by resonance in parallel wires. The wave-length on the wires is inversely proportional to the square root of the dielectric constant of the surrounding medium provided conductivity effects may be neglected. This method may be used at very high frequencies (greater than 3×10^8 sec^{-1}) in connection with spark oscillators, but it requires considerable amounts of material and its accuracy is not very great.[4]

A modification of this method, developed by Drude, requires much less material; but the accuracy is no greater than that of the original method and there is the disadvantage that the appratus must be calibrated with known liquids.[5]

One of the earliest of the electrostatic methods is based on a comparison of the attraction between the plates of a condenser charged to a given difference of potential and separated first by air and then by the unknown liquid. The magnitude of the attraction is proportional to the dielectric constant of the medium between the plates. The method has been used successfully with direct and alternating sources of e.m.f. The only apparent objection to it is that it is inconvenient for small amounts of material.[6]

A modification of this method makes use of the torque acting on a small conducting body (Fürth gives this body the form of an ellipsoid of revolution) suspended in the field between the plates of a condenser. The magnitude of this torque is a function of the dielectric constant of the medium separating the plates.[7]

Harrington, Phys. Rev. **8,** 581 (1916) on water. More recently it has been used by C. P. Smyth, Journ. Amer. Chem. Soc. **49,** 1030 (1927), **50,** 1536 (1928), in the study of organic liquids and liquid mixtures; also by Sack, Phys. Zeits. **28,** 199 (1927) in the study of salt solutions.

[4] This method is based on the work of Lecher and of Blondlot on waves in wires. It was first used by Cohn u. Heerwagen, Wied. Ann. **43,** 343 (1891), and later more extensively by Drude, Wied. Ann. **55,** 633 (1895); **58,** 1 (1896); **59,** 17 (1896). See also Zeits. f. Phys. Chemie **23,** 270 (1897). It has also been used by Marx, Wied. Ann. **66,** 603 (1898), Colley, Phys. Zeits. **10,** 471 (1909); **10,** 657 (1909); **11,** 324 (1910), Rudop, Ann. d. Physik **42,** 489 (1913), Weichman, Phys. Zeits. **22,** 535 (1921), and Mie, Phys. Zeits. **27,** 792 (1926), for the most part on water. It has been applied by Deubner, Ann. d. Physik **84,** 429 (1927) to the study of dilute aqueous salt solutions.

[5] This method is described by Drude in Zeits. f. Phys. Chemie **23,** 270 (1897). The value of the dielectric constants for a large number of substances obtained by the two methods are given. The method has been employed recently by R. Fürth, Ann. d. Physik **70,** 63 (1923) for the study of several organic and biological substances, and still more recently by Voigt, Zeits. f. Physik **44,** 70 (1927) for obtaining measurements on dilute salt solutions.

[6] Much of the early work on water and other liquids was carried out by this method: Cohn and Aarons, Wied. Ann. **33,** 14 (1888); Tereschin, Wied. Ann. **36,** 792 (1888); Heerwagen, Wied. Ann. **49,** 272 (1893); Franke, Wied. Ann. **50,** 163 (1893). More recently Carman, Phys. Rev. **24,** 396 (1924) has revived the method and used it on water at a frequency of 60 cycles. Schmidt, Phys. Rev. **30,** 925 (1927), following the procedure of Carman, has applied it to dilute salt solutions.

[7] The method was used at the suggestion of Nernst by Smale, Wied. Ann. **57,** 215 (1897)

A reflection method using polarized waves of very short wave-length (about 3 cm) has been used by Cole[8] and Merczing[9] to study the absorption bands of water. It is very inexact and of doubtful validity.

There is a very accurate method based on the principle of standing waves in wires described by Drake Pierce and Dow in a preceding paper of this journal. This method however requires very large amounts of material and is for this reason unsuited to the present requirements.

There is lastly another form of resonance method, which is of more interest in the present connection. A circuit, which we will call the *resonator*, containing the unknown, is brought to resonance with an *oscillator*, maintained at a fixed frequency, by adjustment of a variable condenser. This condenser is calibrated and placed in parallel with the cell or fixed condenser for the unknown, and from its settings when the cell is filled first with air and then with the unknown, the dielectric constant of the latter is calculated. Unfortunately this method is unsatisfactory at high frequencies, owing to stray capacity effects in the resonator. These increase with the frequency and may be expected to change with adjustments of the variable condenser. They can never be determined directly and can only be allowed for by calibration of the whole resonator in terms of known liquids introduced into the cell. This procedure, however, has the following disadvantages: (1) it limits the accuracy and range of all new determinations to that of previous measurements of the standard liquids; (2) it is impossible to get good standards of high dielectric constants (greater than about 30) since water itself is not known to great accuracy; (3) it is constantly necessary to check up on the calibration of the circuit.[10]

In order to avoid these difficulties and at the same time profit by the accuracy with which it is possible to make settings by a resonance method it was suggested to me by Professor G. W. Pierce that it might be possible to make a small, rigid resonator which could be entirely immersed in the liquid to be studied, so that all capacities of the circuit would be included alike in the medium. The plan then demands an inversion of the usual procedure of tuning the resonator to the oscillator; instead of this, the frequency of the oscillator is to be varied until it corresponds with the natural period of the resonator, first in air, then in the liquid. These frequencies can then be used to obtain the dielectric constant.

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on water. It has been discussed at length by Fürth, Zeits. f. Physik **22,** 98 (1924). Peckhold, Ann. d. Physik **83,** 427 (1927), has employed it in the study of salt solutions.

[8] Cole, Wied. Ann. **57,** 290 (1896).

[9] Merczing, Ann. d. Physik **33,** 1 (1910); **34,** 1015 (1911).

[10] Resonance methods of this type have been used by the following observers: Thwing, Zeits. f. Phys. Chemie **14,** 286 (1894); Niven, Proc. Roy. Soc. **85A,** 139 (1911); Hyslop, and Carman, Phys. Rev. **15,** 243 (1920); Preuner and Pungs, Phys. Zeits. **20,** 543 (1919); Jackson, Phil. Mag. **43,** 492 (1922); Lattey, Phil. Mag. **41,** 829 (1921); Kerr, Journ. Chem. Soc. **128,** 2796 (1926); Williams, Journ. Am. Chem. Soc. **48,** 1888 (1926) and later; Fritts, Phys. Rev. **23, 345** (1924); Walden, Ulrich, and Werner, Zeits. f. Phys. Chemie **115,** 177 (1925); Kjansky, Zeits. f. Physik **52,** 743 (1928); Hellmann and Zahn, Ann. d. Physik **86,** 687 (1928) and Kniekamp, Zeits. f. Physik **51,** 95 (1928) discuss the method.

After a certain amount of experimentation it was found possible to build compact all metal resonators having natural periods of the desired magnitude. The period of a resonator diminishes with its size, and for a given resonator the period is of course greater in liquids of high dielectric constant. Resonators having a frequency of about 10^8 sec^{-1} in water are small enough to be satisfactorily immersed in 15–20 cc of liquid. This amount of liquid is found to include enough lines of force so that the results are unaffected by parts of the field not included.

The question now arises as to the relation between the natural period of a resonator and the dielectric constant of the medium surrounding it. It is of course well known that if we can treat a circuit as composed of lumped capacity C, inductance L, and resistance R, arranged in series, it will have an impedance given by

$$(R^2+(L\omega-1/C\omega)^2)^{1/2}.$$

This will be a minimum at a frequency, called the resonant frequency, given by

$$\omega=1/(LC)^{1/2}$$

corresponding to the natural period of the circuit.[11] If C_0 is the capacity of the circuit in air, and C_1 its capacity in a medium of dielectric constant ϵ, then

$$C_1=\epsilon C_0.$$

If ω_0 and ω_1 give the corresponding natural periods, then, since L is constant,

$$\epsilon=\omega_0^2/\omega_1^2. \qquad (1)$$

If we could regard our resonators as circuits of lumped capacity, inductance, and resistance, this would make the determination of the dielectric constant

TABLE I. *Dielectric constant ϵ of distilled water.*

Type of Resonator	Temp.	Frequency	ϵ	ϵ*25°
Spiral	21.2	8.147×10^7	79.99	78.62
Cylinder	36.9	4.331×10^7	74.65	78.70
Spiral	38.2	4.344×10^7	74.06	78.51
Cylinder	25.0	2.230×10^7	78.49	78.49
Cylinder	21.3	0.9820×10^7	79.75	78.42
Cylinder	20.0	0.3698×10^7	80.29	78.49
(Cylinder	18.4	0.1396×10^7	84.8	82.4)
				Av. 78.54

* Calculated from temperature data given below.

by the proposed plan very simple. Now there is evidence, to be given below, that we cannot make such an assumption about the resonators; nevertheless

[11] We use ω for convenience. It is to be noted that ω, the natural period T, the resonant frequency f, and the corresponding wave-length λ in free space are given by the relations $\omega/2\pi=f=1/T=3\cdot 10^8\lambda$.

it appears that, if we can neglect the conductivity of the medium, we can still use Eq. (1) to compute the dielectric constant. The justification of this lies in the fact that the results obtained on water with the use of this assumption are consistent among themselves and agree with other observations. The measurements on water were made at various frequencies with a variety

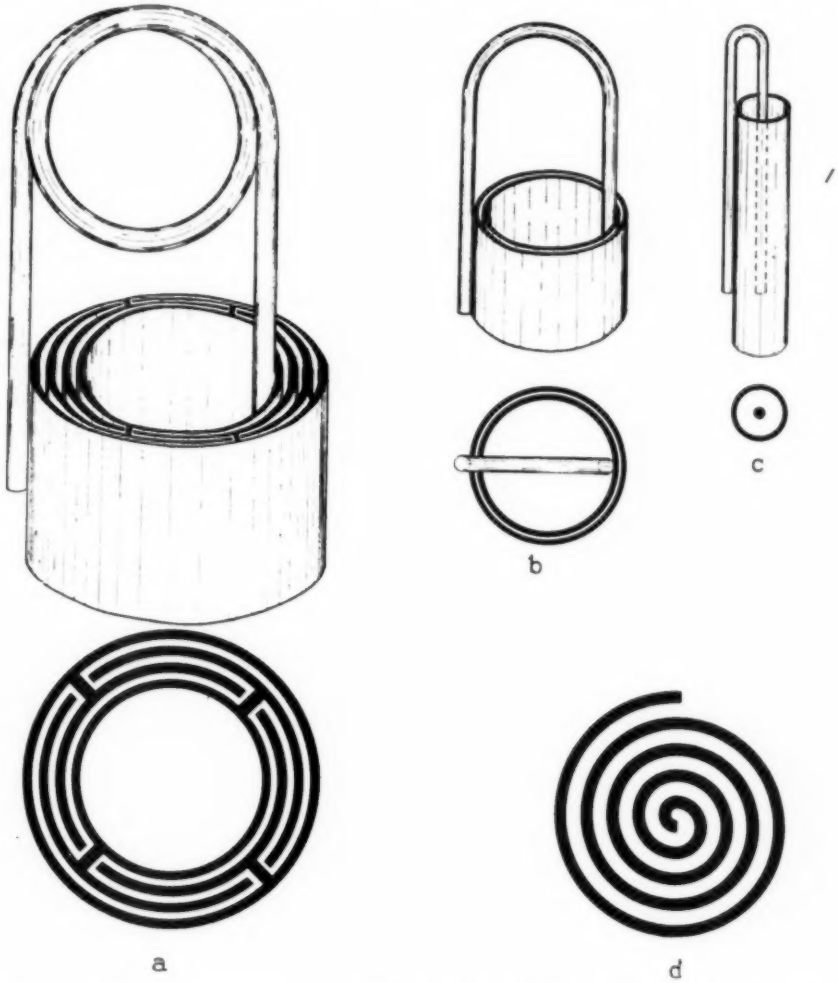

Fig. 1. Types of resonators. a, cylinder type: natural period in air, $8 \cdot 10^{-8}$ sec.; size 13×20 cm. b, cylinder type: natural period, 10^{-8} sec.; size 5×7 cm. c, cylinder type: natural period, $2 \cdot 10^{-9}$ sec.; size. 8 · 6. cm. d, spiral type: natural period, 10^{-9} sec.; diameter, 1.7 cm.

of resonators. Some of these had the form of concentric cylinders and others of spirals. (See Fig. 1.) The results obtained are given in Table I. The values of E were calculated from the observed frequencies by Eq. (1). With one exception they are all in agreement within the experimental error of the determination of the frequencies, and they also agree with values obtained by other methods. The one exception is in the case of the result obtained with

the largest resonator of all at a relatively low frequency. There is no doubt that the discrepancy in this case is due to the effect of conductivity which increases with decreasing frequency and may be expected on theoretical grounds to become evident at about this frequency for water. This close agreement in the values of ϵ is certainly a justification of the application of Eq. (1) to calculate the dielectric constant from the frequency in cases where conductivity of the dielectric may be neglected.

It should be observed in connection with this procedure that it is not possible in all cases to determine $\omega_0 = 2\pi f_0$ directly. If f_1, the frequency of the resonator in water, is greater than about 1.4×10^7, $f_0 = \epsilon^{1/2} f_1$ is greater than about 12×10^7 and lies above the upper range of the oscillator—about 12×10^7. In such cases, however, it is easy to obtain f_0 by determining f_l, the frequency of the resonator in any intermediate liquid l, whose dielectric constant is immediately measured by a larger resonator for which f_0 is known directly. This liquid may be chosen as having low conductivity, and so introduces no trouble on that ground. It need have no especial purity or composition, since its dielectric constant is determined for the occasion. This practice was made use of in determining the values of f_0 for the smaller resonators and is involved in the above determinations of ϵ for water at the higher frequencies. The auxiliary liquid employed was acetone or a mixture of acetone and gasoline. Of course it is evident that each additional measurement of a frequency introduces errors which are accumulated in the final result and such extra steps are to be avoided if possible.

There is no need to describe the vacuum tube oscillator in detail. It was built about a 299X Cunningham tube with the base removed for operation at higher frequencies. The oscillation was set up between the plate and the grid; its frequency was controlled by interchangeable inductances and a rotating condenser driven by a reducing gear and equipped with a dial bearing a vernier. At the lowest frequencies a Hartley circuit was sometimes employed.

The frequency of the oscillator was determined in terms of the frequency of a quartz crystal according to a method described by Pierce.[12] The oscillator was permanently coupled, inductively, with the crystal circuit so as to give audible beats whenever set to the frequency of one of the harmonics of the crystal. These harmonics serve as standard frequencies and are identified by means of a wave meter. From the dial readings of the oscillator corresponding to several nearby harmonics of the crystal, the frequency corresponding to any intermediate setting of the oscillator may be determined by graphical interpolation. The frequency of every setting of the oscillator during the course of a measurement was always obtained directly in this way.

In the above measurements the criterion for resonance was maximum reaction of the resonator on the oscillator. The resonator, suspended by a fine thread in the medium in question, is placed in the field of the oscillator at a distance of 15 to 50 cm from its coil. The frequency of the oscillator is then varied until there is a sudden drop, or rise, in the plate current. This

[12] Pierce, Proc. Amer. Acad. Arts and Sciences **59**, No. 4 (1923).

effect on the plate current of the oscillator undoubtedly accompanies a sharp change in the oscillatory current itself and is taken as the indication of maximum reaction. The corresponding frequency of the oscillator is then determined, according to the method just described, without altering the positions of resonator or oscillator. That in the case of water, or any medium whose conductivity may be neglected under the conditions of measurement, the frequency giving maximum reaction back on the oscillator is the same which gives maximum current in the resonator, corresponding to Eq. (1), was determined by means of a resonator containing a hot wire element (described below). It was found in a test case with water that maximum current was induced in the resonator at a wave-length $\lambda = 5.125$ M; whereas maximum reaction on the oscillator occurred at $\lambda = 5.124$ M. This result accords with the applicability of Eq. (1) to settings obtained by the reaction method.

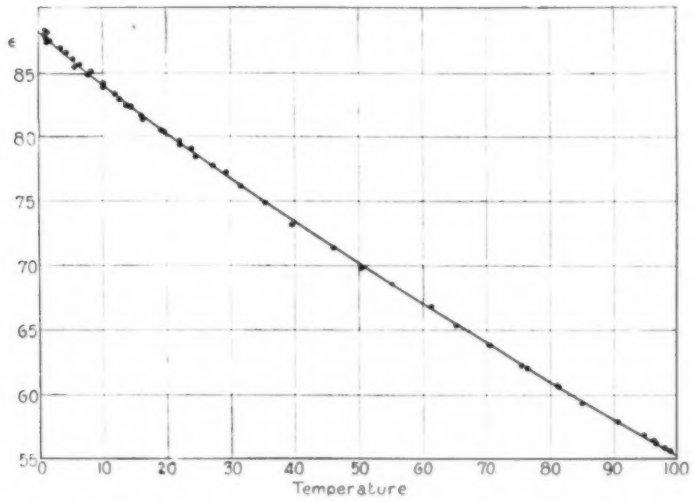

Fig. 2. The dielectric constant of water (ϵ) as a function of temperature.

The sharpness of any resonance setting is of course greater the lower the conductivity of the medium in question. In the case of distilled water the accuracy of a resonance setting at a frequency greater than about 4×10^8 is nearly equal to the accuracy of the determination of the frequency—that is, good to about 0.02 percent. The accuracy of the determination of the resonance frequency itself is thus about 0.04 percent. Any determination of the dielectric constant of water involves the determination of not less than two resonance frequencies, one in air and one in water. The best individual values of the dielectric constant of water obtained by this method are therefore accurate to about 0.1 percent.

The study of water was extended over a range of temperature from about 0°C to 100°C. The results are shown graphically in Fig. 2. The value of the dielectric constant as a function of temperature is expressed with an accuracy equal to that of the experimental results by the equation

$$\epsilon = 78.54[1 - 0.00460(t - 25) + 0.0000088(t - 25)^2] \qquad (2)$$

It is gratifying that these values are in good agreement with those obtained by Drake, Pierce, and Dow (preceding paper) over the range of temperature covered by these observers. They are also in reasonably good agreement with the results of earlier observers given in The International Critical Tables.

We now come to the results obtained on dilute salt solutions where conductivity effects are appreciable. Here the situation is much more complicated and shows (1) that the frequencies corresponding to maximum current in the resonator and maximum reaction on the oscillator are different when the conductivity of the dielectric is appreciable, and (2) that the resonators cannot in general be treated as circuits of lumped capacity, resistance, and inductance.

The evidence to support the above statements comes from the use of resonators, already referred to, containing a hot wire element. These resonators are of the cylindrical type. A small section of the metal loop joining the

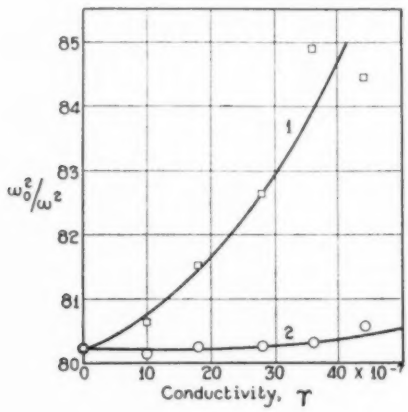

Fig. 3.

two cylinders is removed and replaced by a condensite tube of the same size. This serves to hold the two halves of the resonator rigidly in their former position and at the same time to enclose a piece of 40 gauge copper wire which connects the two cut ends of the loop and restores the connection in the circuit. To the midpoint of this wire are welded the ends of two lengths of 40 gauge wire, one copper and one constantan, which enter through the walls of the tube. These form one junction of a thermo-couple, which is a sensitive detector of any current in the resonator. If the resonator is suspended in water and placed at a distance of two feet from the coil of a power oscillator tuned to the right frequency, sufficient heat is developed in the hot wire to give a full scale deflection of a table galvanometer.

With such a resonator it is possible to tune the oscillator to give either maximum current in the resonator or maximum reaction back on the oscillator. As we have already seen, the two settings are identical for water at a frequency of about $6\times10^7(\lambda=5$ M.) When, however, we turn to dilute salt solutions at about the same frequency, the two methods of tuning no longer

give identical results. Instead, the frequency required to produce maximum current in the resonator is greater than that required for maximum reaction on the oscillator, and the difference between the two increases with the conductivity of the solution. This is shown by the results given in Fig. 3. The upper curve corresponds to maximum reaction; the lower to maximum current. It should be noted that a power oscillator was used to get settings by the first method, and the small oscillator to get settings by the second method.

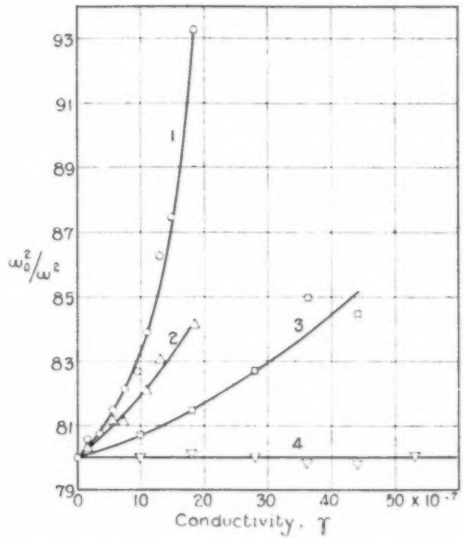

Fig. 4. Values of ω_0^2/ω^2 at varying conductivities obtained by the reaction method of determining resonance. Each curve was made with a different resonator. The natural periods in air of the corresponding resonators, expressed in seconds, are: 1, $11.40 \cdot 10^{-9}$; 2, $5.060 \cdot 10^{-9}$; 3, $1.914 \cdot 10^{-9}$; 4, $1.373 \cdot 10^{-9}$.

Such results are not unexpected in a general way. Suppose we have two circuits 1 and 2, 1 being the oscillator and 2 the resonator. We assume that the circuits are coupled inductively, and that the oscillator is subjected to an impressed E.M.F. of amplitude

$$E = e^{j\omega t}$$

Then, if $Z_1 = R_1 + jX_1$ is the impedance 1, $Z_2 = R_2 + jX_2$ the impedance of 2, and M the mutual induction between them, the complex current amplitudes are given by

$$A_1 = E/[Z_1 - (Mj\omega)^2/Z_2]$$

$$A_2 = A_1 Mj\omega/Z_2.$$

In determining the condition for A_2 maximum, we may certainly neglect changes in A_1, if circuit 1 is a power oscillator. The frequency ω_2 corresponding to A_2 maximum is then seen to be given by the equation

$$\frac{d}{d\omega}\left(\frac{(R_2^2+X_2^2)^{1/2}}{\omega}\right)=0. \qquad (3)$$

The determination of ω_1, corresponding to A_1 maximum, is far less simple, but in general we may expect ω_1 and ω_2 to be different. It is suggestive, however to observe that in the case of a resonator of lumped capacity, inductance, and resistance immersed in a non-conducting medium, we may expect ω_1 and ω_2 to be equal. In this case the impedance of the resonator is $R+j[L\omega-(1/C\omega)]$. Conductivity of the dielectric being negligible, R is simply the resistance of the all-metal circuit, and may be neglected in comparison with L and C. ω_2 is then found to be equal to $1/(LC)$.[1/2] If, on the other hand, we assume that the condition for A_1 max. is governed primarily by the second term in the denominator, we find that ω_1 is also equal to $1/(LC)^{1/2}$, provided we again neglect R in comparison with L and C.

It is, however, as we have pointed out, impossible to regard the resonators as circuits of lumped capacity, inductance, and resistance when conductivity is appreciable. We will now, in conclusion, consider this point. Values of ω_0^2/ω^2, the apparent dielectric constant, for dilute salt solutions of various concentrations obtained by the two methods of determining resonance

TABLE II. *Values of ω_0^2/ω^2 for solutions of potassium chloride at 20°C.*

Resonator 1: $T_0=1.914\cdot10^{-9}$ sec.

% conc. KCl	$\gamma\cdot10^{-7}$	ω_0^2/ω^2	$f(h)$	$f(h)^2\omega_0^2/\omega^2$
0.000	0.3	80.22	1.000	80.22
.005	10.	80.16	1.001	80.32
.010	18.	80.28	1.001	80.44
.015	28.	80.29	1.004	80.73
.020	36.	80.32	1.006	81.28
.024	44.	80.60	1.009	82.06
.029	53.	80.76	1.013	82.86
.034	62.	80.81	1.017	83.56

Resonator 2: $T_0=2.495\cdot10^{-9}$ sec.

% conc. KCl	$\gamma\cdot10^{-7}$	ω_0^2/ω^2	$f(h)$	$f(h)^2\omega_0^2/\omega^2$
0.000	0.3	80.22	1.000	80.22
.005	10.	80.19	1.001	80.35
.010	18.	80.01	1.003	80.49
.015	28.	80.62	1.006	81.59
.020	36.	80.62	1.010	82.23
.024	44.	80.89	1.015	83.31

Resonator 3: $T_0=6.629\cdot10^{-9}$ sec.

% conc. KCl	$\omega\cdot10^{-7}$	ω_0^2/ω^2	$f(h)$	$f(h)^2$
0.000	0.3	80.22	1.000	80.22
.001	2.	80.22	1.001	80.38
.002	4.	80.09	1.001	80.25
.003	6.	80.17	1.002	80.49
.004	8.	79.86	1.004	80.50
.005	10.	79.70	1.005	80.50
.006	11.	79.89	1.007	81.02
.008	15.	79.31	1.012	81.22
.010	18.	78.47	1.017	81.15
.012	22.	78.12	1.025	81.11

are shown graphically in Figs. 4 and 5. The values obtained by the reaction method are in general higher than those from the thermal procedure and both sets of results vary among themselves. We will discuss only the latter, where the theory is far simpler. These are given in Table II.

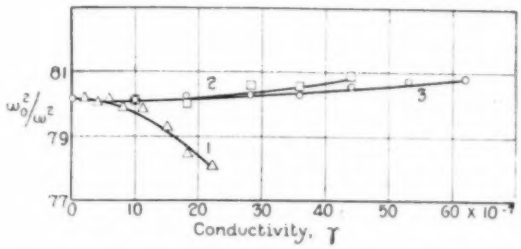

Fig. 5. The same, obtained by the thermal method. Corresponding natural periods in air are: 1, $6.629 \cdot 10^{-9}$; 2, $2.495 \cdot 10^{-9}$; 3, $1.914 \cdot 10^{-9}$.

Let us consider the behavior of an ideal resonator of lumped capacity, inductance, and resistance and compare the predictions with the results given above. Such a circuit placed in a conducting dielectric will behave as if the plates of the condenser were short circuited by a resistance r. If R denote the resistance of the metallic part of the circuit as before, and C and L its capacity and inductance, then it can be shown that the impedance of the circuit suspended in the conducting dielectric is

$$R+\frac{r}{1+r^2C^2\omega^2}+j\left(L\omega+\frac{r^2C\omega}{1+r^2C^2\omega^2}\right).$$

The frequency corresponding to maximum current amplitude in the resonator may be obtained from Eq. (3) and is given by

$$\omega^2=\frac{1}{2LC}\left(1\pm\left(\frac{2LC}{r^2C^2}+1\right)^{1/2}\right),$$

provided we neglect the ratio R/r. Now it can be further shown that for any condenser filled with a medium of dielectric constant ϵ and conductivity γ, the equivalent resistance r between the plates is given by

$$rC=\epsilon/4\pi\gamma.^{13}$$

Therefore, taking account of the fact that $C=\epsilon C_0$, where C_0 is the capacity of the resonator in air, and that $1/C_0L=\omega_0^2=4\pi^2/T_0^2$, where T_0 is the natural period of the resonator in air, we obtain finally

$$\frac{\omega^2}{\omega_0^2}=\frac{1}{2\epsilon}\left\{1\pm\left(1+\frac{2}{\epsilon}(2T_0\gamma)^2\right)^{1/2}\right\}.$$

Since if $\gamma=0$ this must reduce to $\omega^2/\omega_0^2=1/\epsilon$, we discard the $-$ sign before the radical. This result may be compactly expressed by

$$\omega/\omega_v=f(h)/\epsilon$$

[13] I am indebted to Professor Pierce for this result.

where $f(h)$ has been tabulated for values of h.[14] If $h=0$, $f(h)=1$. If h is less than about 0.12, $f(h)$ is not greater than 1.001, and ω_0^2/ω^2 is equal to ϵ to an accuracy of 0.2 percent or better.

For distilled water where $\gamma=3\times10^6$ e.s.u., approximately, we should be able to express ϵ by ω_0^2/ω^2 to an accuracy of 0.2 percent in the case all measurements for which T_0 (corresponding to ω_0) is less than 10^{-7} secs, or for which λ_0, the corresponding wave-length in free space, is less than 30M. For liquids, e.g. salt solutions, for which γ is greater, $f(h)$ increases more rapidly with T_0 and we should be obliged to use smaller resonators having higher natural periods. But the main thing to notice is that as $T_0\gamma$ becomes appreciable and increases, ω_0^2/ω^2 becomes increasingly less than ϵ, according to Eq. (4).

If we attempt to correct the experimental values according to Eq. (4), we obtain the results given in the last column of Table II. Now it is pretty clear that these corrected results cannot give the true values of the dielectric constants of the solutions. The reason for this is that if they did, we should be obliged to assume the dielectric constant to vary with the frequency over the range covered by the measurements and to be greater than that of pure water. The results of Drake, Pierce, and Dow, however, show that the dielectric constant of dilute salt solutions is independent of frequency over the range in which we are interested and is in fact the same as that of water to an accuracy of about 1 percent up to a concentration of 1/70 normal KCl. These results are obtained by a method in which the theory is much simpler and the correction factor known. We are therefore justified in concluding that although the resonators may be treated as circuits of lumped capacity, inductance, and resistance in cases where the conductivity of the dielectric is negligible, i.e., where $T_0\gamma$ is small, they do not in general have the properties of such circuits, but behave in a much more complicated way. It is possible indeed that they are rather to be regarded as lines, if of a complicated type. The analysis of the behavior of even the simplest types of lines is, however, very complex under the circumstances of the above measurements and no attempt has been made to carry it out.

In any case, from the experimental results on the salt solutions, it is clear that we can use ω_0^2/ω^2 directly to express ϵ in the case of frequencies determined by the thermal method up to conductivities many times that of water, provided we use resonators having small natural periods. Table II shows that anomalies begin to appear at condutivities corresponding to values of $T_0\gamma$ for which the correction term $f(h)$, obtained from the analysis of the ideal circuit, begins to become significant. This is not unexpected. It appears that we are safe in equating ω_0^2/ω^2 and ϵ for values of h not greater than about 0.1. This means that if we use a resonator having a natural period in air of about 10^{-9} sec, we can employ the method up to conductivities about 100 times that of water. On the other hand if we make settings by the reaction methods we run into difficulties considerably sooner. Here we are probably safe up to conductivities 20–30 times that of water.

[14] G. W. Pierce, Proc. Amer. Acad. Arts and Sci. **57**, No. 7 (1922).

ON THE ANOMALOUS ROTATION OF THE SUN*

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Abstract

The requirements of Jeans' theory of the anomalous solar rotation are not in accord with the facts of solar magnetism. A new theory is worked out which attributes the anomaly to atmospheric motions arising from the interaction of ions with the solar magnetic field and an assumed electric field. Observations of the solar atmosphere are made only in those regions where the gaseous pressure is such that the ion free paths are long. Ions of both kinds which execute long free paths in crossed electric and magnetic fields are swept in the same direction and give rise to a mass motion. This superimposed drift of the solar atmosphere is shown to account for the rotational anomaly and the calculated variation of the angular velocity with latitude is of the observed form. The theory requires that the sun possess a radial electric field having a sign and distribution similar to that observed on the earth.

IT HAS been known for nearly 100 years that the measured rotational period of the sun depends upon the latitude of the point selected for observation and that it varies from 25 days at the equator to over 30 days at the pole. Moreover, the value of the period at any given place seems to depend somewhat on the level of the point observed. It has been found that in the solar reversing layer the measured angular velocities at low latitudes, expressed in degrees per day, were given approximately by the relation

$$W = 14^\circ.54 - 3^\circ.50 \sin^2 \lambda \qquad (1)$$

where λ is the latitude.

Jeans[1] has proposed a theory to account for the rotation phenomena and he attributes the effects to the braking action of the radiation which filters through the outer solar layers. The final form of his theory requires that the central regions of the sun rotate from ten to fifty times faster than the surface layers and that these layers play only a minor part in the transfer of the radiated angular momentum. It is difficult to establish the existence of high rotational velocities inside the sun from theoretical considerations and it now appears that such a rotation may be improbable. The essential characteristics of the solar magnetic field are known from the work of Hale and his collaborators at Mt. Wilson[2,3] Observatory. This work established the fact that the distribution of the solar magnetic field at any given level was similar

* Released by the Navy Department.

[1] Jeans, Astronomy and Cosmogony, Cambridge Press, 1928.

[2] Hale, Astrophys. J. **38**, 31 (1913).

[3] Hale, Sears, van Maanen and Ellerman Astrophys., J. **49**, 1 (1918).

to that of the earth; that the field was limited radially and that the magnetic pole did not coincide with the geographic pole but rotated about it with a period of 31.4 days. These magnetic facts suggest that Jeans' theory of the anomalous solar rotation is incorrect, for if we assume that the rotational velocity changes from layer to layer as we go outward from the core of the sun, then the motion of the magnetic pole with respect to the axis of rotation will set up electrical eddy currents in the moving layers which will tend to bring them into rotational synchronism with the magnetic field. This difficulty would vanish if the magnetic and geographic poles coincided. A still more serious difficulty arises from the fact that on almost any theory of the permanent magnetic field of the sun and earth, as for example, a theory which attributes the field to electrical currents[4,5], the magnetic pole would be expected to rotate with the same period as the entire mass. Superimposed on this might be a slow precession but it is unlikely that the solar fields should behave in a manner essentially different from that observed in the case of the earth whose magnetic poles rotate with the period of the entire mass. It thus seems clear that the rotational period of the entire solar mass is 31.4 days and not one-tenth of this as is required by Jeans' theory. The objections to Jeans' theory are of such a nature that the problem has been re-examined. It has been found possible to account for the observations in a simple manner by considering the electromagnetic reactions of the ions in the solar reversing layer.

Mt. Wilson researches demonstrated that the solar magnetic field is essentially similar to that of a uniformly magnetized sphere whose exterior field is limited by some special mechanism. It has been shown that this limitation of the solar field is adequately explained by the diamagnetic properties[6] of the solar atmospheric ions; for the effective permeability of an ion gas approaches zero under precisely the conditions that exist in the solar reversing layer. It has been argued recently that boundary effects may annul the diamagnetism of the reversing layer, but this view can not be supported. The effect of the boundary has been considered by van Leeuwen[7] for the case of a metal, who found that the current sheet at the boundary is able to compensate for the volume diamagnetic effect under certain special conditions. She considered the case of short free paths and assumed that the free electrons making up the electron gas were reflected specularly when they collided with the boundary. To meet this condition it is necessary that the boundary be sharp and that the component of the electron momentum normal to the boundary be reversed on impact while the tangential component is preserved. The requirement is satisfied when an electron collides with a heavy ion but when an ion collides with a boundary ion or molecule of its own mass, the normal momentum of the colliding ion is not reversed and boundary currents cannot cancel the volume diamagnetism. Ions play an important part in solar dia-

[4] Gunn, Phys. Rev. **34,** 335 (1929).
[5] Gunn, Phys. Rev. **34,** 1621 (1929).
[6] Gunn, Phys. Rev. **33,** 614 (1929).
[7] van Leeuwen, Jour. d. Physique **2,** 361 (1921).

magnetism and it is clear that van Leeuwen's calculations do not apply there. Moreover, we must note that the sun's atmosphere has no outer boundary and the inner boundary is not sharp so that complete compensation is impossible and we are left with the primary effect—diamagnetism. This general conclusion was pointed out clearly enough in the writer's first paper.[8] Chapman[9] has proposed an alternative theory of the radial limitation of the magnetic field but the author has shown[10] that the effect he invokes to explain the phenomena is largely cancelled by another effect which arises from the inhomogeneity of the impressed magnetic field. Moreover, Chapman's theory encounters a serious qualitative difficulty in that the gravitational drift currents of the type he postulates become very small at high solar latitudes where the magnetic field intensity becomes large and nearly parallel to the gravitational acceleration. Thus his theory leads to the conclusion that the magnetic field at a given level near the poles should be much larger than is observed and that a large unobserved stray magnetic field should exist. Diamagnetism on the other hand is equally effective at the poles as at the equator and predicts the same fractional reduction of the initial field at a given ion pressure. This is in accord with observation.

The existence of diamagnetism in the reversing layer and direct spectrosopic evidence both show that the ion free paths in the reversing layer must be longer than the critical free path; that is, they are longer numerically than the radius of the helix generated by the ion as it is caused to spiral about the impressed magnetic field. When this condition is satisfied, other important motions of the nature of ion drifts arise from a combination of an impressed magnetic field with other types of field. These drifts may result from a magnetic field crossed with a gravitational field[11,12], an inhomogeneous magnetic field,[10] or an electric field.[8] The ion drifts and their possible effects have been investigated elsewhere; it is only of importance to note here that the first two effects give rise to ion drifts which are opposite in direction for the positive and negative ions and hence constitute a current while the electric field crossed with a magnetic field acts in such a way as to urge both ions in the same direction and hence is of the nature of a mass movement. When the free paths of the ions and electrons are both longer than their respective critical free paths both drift in the same direction with the same velocity. In certain unobserved regions of the solar atmosphere, however, the free paths of the electrons are longer than their critical radius while the free paths of the ions are less than their own critical value. Thus in this special region electric currents flow which may tend to magnetize or demagnetize the sun according to the direction of the impressed electric field. Such currents may be important in theories of sunspots or of the limitation of the solar magnetic field,

[8] Gunn, Phys. Rev. **32**, 133 (1928).
[9] Chapman, Monthly Notices **89**, 57 (1928).
[10] Gunn, Phys. Rev. **33**, 832 (1929).
[11] Hulburt, Phys. Rev. **33**, 412 (1929).
[12] Chapman, Monthly Notices **89**, 57 (1928).

but it is to be noted that the conductivity of this narrow region is moderately large and any electric field must necessarily be small. Our greatest interest in the present paper is in the mass motions of the atmosphere and we therefore assume the sun to have electric as well as magnetic fields and will consider their joint mechanical effects. At the solar equator the direction of the magnetic field is tangential and that of any electric field must be radial. These crossed fields give rise to an equatorial ion drift which is in the same direction for both types of ions and is independent of the charge or mass of the ion. Were neutral molecules present they would presumably be swept along by occasional collisions with ions. It thus seems possible that the observed anomalous rotation of the sun is an effect arising from the movement of the solar atmosphere and is not due to deep seated circulation which seems to be required in earlier ideas regarding the phenomena.

The problem of the electrical state of a rotating heavenly body has been considered by several writers[13,14,15] and the electrical charge distribution worked out under special assumptions. For example, Rosseland[13] has pointed out that in the stars loss of charge by radioactive processes might be expected. In addition we may have electrical fields arising from a separation of charge due to (*a*) gravitational fields[16] (*b*) temperature gradients (*c*) radiation pressure (*d*) pressure gradients[13] (*e*) motion in a magnetic field.[15] It seems probable that in the reversing layer (*a*), (*b*), and (*c*) are small compared to the electric fields arising from other causes. A study of the electric fields ar sing from the motion of the earth in its own magnetic field has been made by Page[15] who assumed that the earth was a uniformly magnetized conducting sphere. Upon working out the consequences of his assumptions he found that electric fields are set up in the high atmosphere which have values such that the ions are swept to the westward with a velocity of the same order of magnitude as the peripheral velocity of the earth. An observer outside the earth watching the ions in the high atmosphere would thus observe an apparent rotational period greater than 24 hours. The entire calculation may equally well be applied to the sun and correction made for the change of magnitude of the quantities due to a larger field and a different type of magnetic distribution. This readjustment does not greatly alter the situation and if the sun is assumed to be unchanged as a whole and free of electric fields in the reversing layer, except those arising from the solar rotation, then an observer on the earth watching an equatorial point in the reversing layer would observe a period of rotation for the layer which is greater than the period of rotation as indicated by the motion of the magnetic pole. This is not in accord with observation and we must conclude that radial electric fields other than that due to rotation in its own magnetic field exist in the solar reversing layer. We shall not enter into a discussion as to the origin of this electric field but simply point out that observation demands its existence. Moreover, as we

[13] Rosseland, Monthly Notices **84,** 720 (1924).
[14] Rosseland, Astrophys. J. **62,** 387 (1925).
[15] Page, Phys. Rev. **33,** 823 (1929).
[16] Pannekoek, Bull. Astro. Inst. Netherlands 19, (1922).

shall see presently, the electric field required is in the same direction, is much smaller, and varies radially in substantially the same manner as the observed electric field of the earth. It is thus consistent with such astrophysical data as are available at the present time.

The mean drift velocity $\boldsymbol{u}$ imposed on both kinds of ions which execute long free paths in crossed electric and magnetic fields is given by

$$\boldsymbol{u}=\frac{\boldsymbol{E}\times\boldsymbol{H}}{H^2}=\frac{E}{H}\sin\beta. \tag{2}$$

Where E and H are in e.m.u. and β is the angle between E and H. We will take H positive northward in the reversing layer at the equator since it coincides in direction with the rotational velocity of the sun and E radially outward. Under this condition a positive value of $\boldsymbol{u}$ corresponds to a westward velocity relative to the surface. According to Mt. Wilson data[2,3] the magnetic field H at a given atmospheric level and latitude λ is given by

$$H=H_0(1+3\sin^2\lambda)^{1/2} \tag{3}$$

where H_0 is the value of the equatorial field at the level considered. Thus combining (1) and (2) the superposed angular velocity ω at a given level which arises from the velocity of drift is

$$\omega=\frac{E\sin\beta}{H_0R[(1+3\sin^2\lambda)(1-\sin^2\lambda)]^{1/2}} \tag{4}$$

where R is the radius of the sun. The diamagnetic layer of the solar atmosphere distorts the permanent magnetic field and the value of β is not readily determined. It is convenient to note that due to diamagnetism the magnetic field is nearly parallel to the surface of the sun in a region 30° on each side of the equator (say) and that the electric field must be radial, so that within the range specified an expansion of Eq. (4) is valid and we may also set $\sin\beta=-1$. Making this substitution, expanding (4) and retaining only the first two terms we have

$$\Omega=\Omega_0-(E/H_0R)(1-\sin^2\lambda) \tag{5}$$

where Ω is the resultant (observed) angular velocity, Ω_0 the angular velocity as measured by the rotation of the magnetic pole and the last two terms represent the contribution due to the atmospheric drift. In order to account for faster rotation at the equator we must now assume that the required value of E is radially inward or negative. If we set

$$\Omega_0+(E/H_0R)=\Omega_0' \tag{6}$$

then (5) becomes

$$\Omega=\Omega_0'-(E/H_0R)\sin^2\lambda \tag{7}$$

and agrees in form with the observed relation given in Eq. (1). By selection of the correct value for E; Eq. (7) gives the exact relation. Thus from Eq. (1) and (7)

$$(E/H_0R) = 7.06 \times 10^{-7} \text{ rad/sec}$$

and taking $R = 6.95 \times 10^{10}$ cm and $H = 25$ gauss we find $E = 0.013$ volts/cm.

There are no data available which contradict the assumption of a radial electric gradient of 0.01 volt/cm in the observed regions of the reversing layer and unless the atmosphere of the sun rotates slower than the magnetic poles we must assume that some kind of an electric field exists which is directed radially inward. The conductivity of the layer in the direction of the electric field has been shown to approach zero[8] when the electric and magnetic fields are nearly perpendicular as they actually are in the equatorial zone we have considered. There is therefore no reason to suppose that electric charges can readily flow in such a manner as to neutralize the field. Near the poles the electric and magnetic fields approach parallelism and the conductivity increases; thus the electric field distribution in this region is quite different from that at the equator.

The previous calculation of the equatorial electric field was made for an observed level where the magnetic field was taken as 25 gauss. At different values of the magnetic field we might expect different values for the drift velocity. Observations show that deviations do exist but they are not so large that it would be legitimate to assume the electric field constant at all altitudes. A better approximation is suggested by the fact that the drift velocity is observed to be nearly constant with superposed regular variations. On this assumption we have

$$(E/H) = K_1 = 5 \times 10^4 \text{ cm/sec} \tag{8}$$

which requires that E increase with increasing ion pressure in the same manner that H is known to increase. This relation undoubtedly breaks down in the deeper layers of the solar atmosphere. The origin of the electric field is unknown and the distribution cannot now be calculated from independent considerations. The required distribution can be worked out, however, by use of Eq. (8) and earlier results obtained from diamagnetic considerations[10] which gave an approximate relation between the ion density and the magnetic field in the reversing layer. This relation is:

$$N = H^2/4\pi kT \tag{9}$$

where N is the ion density, H the magnetic field intensity, k the Boltzmann constant and T the absolute temperature. By the use of observed values for H it was found that the distribution of N was a logarithmic function of the altitude. Making the further assumption that the solar atmosphere was in gravitational equilibrium it was found that the distribution calculated from magnetic data agreed with that required by a gravitational equilibrium distribution when the mean atomic weight of the particles in the reversing

layer was taken as 3.3. A correction for the presence of an electric field was also made but the calculation is not now believed to be valid. In view of the recent work of Unsöld[17] it hardly seems legitimate to talk of equilibrium in the solar atmosphere but if the values of the ion pressure are averaged over a fairly long period the usual expression probably well represents the distribution. On this assumption the ion density n at any level r is given by

$$n = n_0 \exp\left(\frac{-zm_H g(r-R)}{kT}\right) \tag{10}$$

where n_0 is the number of ions per cm^3 at the "surface" of the sun, z the mean atomic weight of the solar ions and R the radius of the sun. We will follow earlier work and assume that the surface of the sun is located at a level where the free paths of the ions are just equal to the radius of the helix generated by an electron as it is caused to spiral about the impressed magnetic field. Extrapolation has shown that the ion pressure at the surface so defined was nearly one half an atmosphere and that the magnetic field intensity was roughly 12,000 gauss. Below this surface the magnetic field is no longer modified by diamagnetism and the electric conductivity is so large that electric fields are negligibly small compared to those outside. Combining (9) and (10) we have

$$H = H_0 \exp\left(\frac{-zm_H g(r-R)}{2kT}\right) \tag{11}$$

where H_0 is the surface magnetic field intensity. We are now able to calculate the difference of potential between the solar surface and outer space. Let this potential difference be ϕ, then from Eq. (8) we have

$$\phi = \int_R^\infty E dr = K_1 \int_R^\infty H dr. \tag{12}$$

The integration is carried out along a path radially outward at the equator which gives by aid of Eq. (11)

$$\phi = \frac{2K_1 H_0 kT}{zm_H g}. \tag{13}$$

Taking therefore $K_1 = 5\times10^4$ cm/sec; $H_0 = 1.2\times10^4$ gauss; $Z = 3.3$; $m_H = 1.66\times10^{-24}$ gm; $g = 2.7\times10^4$ cm/sec^2; $k = 1.37\times10^{-16}$ and $T = 6\times10^3$ we get $\phi = 6.6\times10^{15}$ e.m.u. or 6.6×10^7 volts. We have pointed out that in the special region where the electron free path is long and the ion free path is short (according to our special definition) the conductivity is moderately large and the electric field must therefore be small. If we assume that the electric field in this region is zero and integrate from the outer edge of the region where H_0 is 280 gauss[4] out to infinity we find the potential difference to be 1.5×10^6

[17] Unšold, Astrophys. J. **69**, 209 (1929).

volts. This is nearly the same potential difference as is observed between the earth and free space. While this calculation cannot be exact since it involves a questionable extrapolation of what may be considered an empirical relation it probably does give a good approximation to the potential difference required to maintain an electric field of the assumed type and distribution.

Special attention should be called to the striking similarity between the the solar magnetic and electric fields and the same fields on the earth. Spectroscopic data show that the solar magnetic field is not unlike that of the earth except for the distortion of the field due to diamagnetic effects in the reversing layer. The requirements in regard to the electric field as deduced in this paper from the observed movements of the solar atmosphere are almost identical with the observed features of the earth's electric field. The earth's electric field in the region of poor electrical conductivity is radially inward, its value drops off with decreasing pressure fairly rapidly in a manner precisely as required in the sun. Moreover the observed potential difference between the surface of the earth and its outer layers is almost identical with that calculated for the sun. The equality of the potentials of the sun and earth seems significant, for conditions on the sun and earth are greatly different and such equality could hardly be expected unless the electric fields arise from the same fundamental mechanism.

A SIMPLE EQUATION FOR THE JOULE-THOMSON EFFECT IN REAL GASES

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Abstract

Simple approximate relations are given for μC_p and the pressure variation of C_p expressing these quantities as functions of the independent variables p and T. They are derived from the usual thermodynamic relations by use of one form of the Beattie-Bridgeman equation of state, which expresses V as an explicit function of p and T. The values of the Joule-Thomson coefficient μ for air and for ammonia calculated from the relations for μC_p and C_p, equations (10) and (4) respectively, agree well with the observed values in the case of air, and fairly well for ammonia.

The approximate equation for μC_p calculates values of the inversion temperatures of the Joule-Thomson effect in air which are in good agreement with the experimental results.

A VERY sensitive test of an equation of state is the accuracy with which the calculated values of the Joule-Thomson coefficient μ and of the inversion temperatures of the Joule-Thomson effect, at which $\mu = 0$, agree with the experimental results. Keyes[1] has shown that the Joule-Thomson effect in air and carbon dixoide can be calculated by use of his equation of state with good success.

Bridgeman[2] has derived expressions from the general thermodynamic relations and the Beattie-Bridgeman[3] equation of state for μC_p and for the pressure variation of the heat capacity at constant pressure, C_p. The values of μ and of C_p for air computed from these relations agree well with those obtained by Roebuck[4] from Joule-Thomson measurements which extend from 0 to 280° C and to 220 atmospheres. The equation of state constants used by Bridgeman in this correlation were determined from the compressibility data of Holborn and Schultze.[5]

The values of μ and of the pressure variation of C_p for ammonia calculated[6] from the expressions obtained by use of the Beattie-Bridgeman equation of state agree well with the experimental results of Osborne, Stimson, Sligh and Cragoe[7] at the higher temperatures, but the deviations become large at the

* Contribution No. 234.

[1] Keyes, Jour. Amer. Chem. Soc. **43**, 1452 (1921); ibid. **46**, 1584 (1924).

[2] Bridgeman, Phys. Rev. **34**, 527 (1929).

[3] Beattie and Bridgeman, Proc. Amer. Acad. Arts and Sci. **63**, 229 (1928).

[4] Roebuck, Proc. Amer. Acad. Arts and Sci. **60**, 537 (1925).

[5] Holborn and Schultze, Ann. d. Physik **47**, 1089 (1915); see also Holborn and Otto, Zeits. f. Physik **33**, 1 (1925).

[6] Beattie, Jour. of Math. and Phys. **9**, 11 (1930).

[7] Osborne, Stimson, Sligh and Cragoe, Scientific Papers of the Bureau of Standards **20**, 65 (1925).

lower temperatures. The equation of state constants for ammonia used in this comparison were determined from the compressibility measurements of Meyers and Jessup,[8] which Cragoe[9] and Osborne, Stimson, Sligh and Cragoe[7] have shown could be correlated, in part, with the thermal data. The large deviations of the values computed by use of the equation of state from the experimental results at the lower temperatures may be due to either or both of two causes: A slight inconsistency between the thermal and compressibility data, or the failure of the equation of state to reproduce all of the trends of the compressibility data near the saturation line. It should be mentioned, however, that the equation reproduces the compressibility measurements of Meyers and Jessup with an average deviation of 0.043 percent.

The equation of state used for these calculations is:

$$p=\frac{RT}{V}+\frac{\beta}{V^2}+\frac{\gamma}{V^3}+\frac{\delta}{V^4} \tag{1}$$

$$\beta=RTB_0-A_0-Rc/T^2$$

$$\gamma=-RTB_0b+A_0a-RB_0c/T^2$$

$$\delta=RB_0bc/T^2$$

where R is the ideal gas constant and A_0, a, B_0, b and c are constants for each gas.

The expressions for μC_p and the pressure variation of C_p used by Bridgeman[3] and by the author[6] can be derived from the usual thermodynamic relations by use of (1). They are:

$$\mu C_p=\frac{\left[-B_0+\frac{2A_0}{RT}+\frac{4c}{T^3}\right]+\left[2B_0b-\frac{3A_0a}{RT}+\frac{5B_0c}{T^3}\right]\frac{1}{V}-\frac{6B_0bc}{T^3V^2}}{1+\frac{2\beta}{RTV}+\frac{3\gamma}{RTV^2}+\frac{4\delta}{RTV^3}} \tag{2}$$

$$C_p=C_{p_0}{}^*-R+(Rc/T^3V)\left[6+(3B_0/V)-(2B_0b/V^2)\right]+\frac{R\left\{1+\left[B_0+(2c/T^3)\right](1/V)+\left[-B_0b+(2B_0c/T^3)\right](1/V^2)-(2B_0bc/T^3V^3)\right\}^2}{1+(2\beta/RTV)+(3\gamma/RTV^2)+(4\delta/RTV^3)} \tag{3}$$

where $C_p{}^*$ is the value of C_p at infinitely low pressures and is a function of the temperature alone. These equations will be called the "complete" relations, since no approximations have been introduced.

Equation (3) can be transformed[10] into the "approximate" expression:

$$C_p=C_p{}^*+\left[(2A_0/RT^2)+(12c/T^4)\right]p; \tag{4}$$

[8] Meyers and Jessup, Refrigerating Engineering **11,** 345 (1925).
[9] Cragoe, Refrigerating Engineering **12,** 131 (1925).
[10] Beattie, Phys. Rev. **34,** 1615 (1929).

in which the independent variables are p and T. This relation represents the heat capacity data on air and ammonia almost as well as the "complete" equation (3).

By use of a suitable approximation,[11] the equation of state (1) can be written so that V is expressed as an explicit function of p and T:

$$V=\frac{RT}{p}+\frac{\beta}{RT}+\frac{\gamma}{R^2T^2}p+\frac{\delta}{R^3T^3}p^2 \tag{5}$$

where β, γ and δ are the functions of the temperature and the equation of state constants given in (1). When the values of the equation of state constants determined for use in equation (1) are substituted into (5), the experimentally measured volumes are calculated very satisfactorily even to 100 atmospheres or over when the temperature is not too near the critical value.

Equation (5) makes it possible to express μC_p and C_p as functions of the independent variables p and T. When the partial differentials in the general thermodynamic ralations

$$\mu C_p=T\left(\frac{dV}{dT}\right)_p-V \tag{6}$$

$$\left(\frac{dC_p}{dp}\right)_T=-T\left(\frac{d^2V}{dT^2}\right)_p \tag{7}$$

are evaluated by (5), and equation (7) integrated between 0 and the variable pressure p, there result:

$$\mu C_p=\left[-B_0+\frac{2A_0}{RT}+\frac{4c}{T^3}\right]+\left[\frac{2B_0b}{RT}-\frac{3A_0a}{R^2T^2}+\frac{5B_0c}{RT^4}\right]p-\left[\frac{6B_0bc}{R^2T^5}\right]p^2 \tag{8}$$

$$C_p=C_p^*+\left[\frac{2A_0}{RT^2}+\frac{12c}{T^4}\right]p+\left[\frac{B_0b}{RT^2}-\frac{3A_0a}{R^2T^3}+\frac{10B_0c}{RT^5}\right]p^2-\left[\frac{10B_0bc}{R^2T^6}\right]p^3 \tag{9}$$

It has been shown[10] that the heat capacity of air and ammonia are fairly well represented by the relation (4) which can be obtained from (9) by dropping all terms of higher powers than the first in p. When a similar approximation is made in (8), we obtain a relatively simple equation for μC_p in terms of the variables p and T:

$$\mu C_p=\left[-B_0+\frac{2A_0}{RT}+\frac{4c}{T^3}\right]+\left[\frac{2B_0b}{RT}-\frac{3A_0a}{R^2T^2}+\frac{5B_0c}{RT^4}\right]p. \tag{10}$$

The comparisons of the values of μ computed by use of the "approximate" equations (10) and (4) with the experimental results for air and ammonia are given in Tables I and II. For these computations the values of C_p^* for air were calculated by use of (4) from the equation[12]

$$C_p=0.2405+0.000019t$$

[11] Beattie, Proc. Nat. Acad. Sci. **16**, 14 (1930).

[12] Holborn, Scheel and Henning, "Wärmetabellen". Vieweg, Braunschweig, 1919; p. 58.

where C_p is the specific heat capacity at one atmosphere in 15° calories per gram per degree centigrade and t is in degrees centigrade; the values of C_p^* for ammonia are given by the expression[7]

$$C_p^* = 1.1255 + 0.00238T + \frac{76.8}{T}$$

where C_p^* is in joules(v) per gram per degree centigrade and T is in degrees Kelvin (°C+273.1).

The units of the equation of state constants and those in which the data are expressed are given in the Tables I and II. In the use of equation(4) the reduction factors calculated from data given in International Critical Tables for the term evaluated from the equation of state are: 0.83605 15°-calories/gram per liter-atmospheres/mole for air, and 0.101293 joules (v) per cm³-atmospheres for ammonia. The values of C_p derived from (4) were then multiplied by the following reduction factors before use in (10): 1.19609 liter atmospheres/mole per 15° calories/gram for air and 7.5030 cm³-meters of mercury per joules (v).

TABLE I. *Comparison of the calculated with the observed values of the Joule-Thomson coefficient for air.*

Calculations made with Equations (10) and (4).
In units of atmospheres, liters per mole and degrees Kelvin ($T°K = t°C + 273.13$) the values of the constants for air are:

$R = 0.08206$, $A_0 = 1.0763$, $a = 0.01697$,
$B_0 = 0.04070$, $b = -0.02174$, $c = 12 \times 10^4$.
Mol. wt. = 28.960.
Observed values are those of Roebuck.

Temp. °C Pressure, atm.		0	25	50	75	100	150	200	250	280
		Joule-Thomson coefficient, $\mu \times 10^3$, degrees C per atm.								
1	obs.	266	227	189	158	133	93	63	40	30
	obs.-calcd.	−8	1	0	−1	−1	−2	−3	−3	−2
20	obs.	249	212	178	149	124	86	56	35	25
	obs.-calcd.	−6	1	1	1	−1	−2	−4	−4	−3
60	obs.	214	182	153	128	106	71	45	25	16
	obs.-calcd.	−5	−1	0	0	1	−3	−4	−4	−3
100	obs.	178	152	128	107	89	59	35	16	8
	obs.-calcd.	−10	−5	−3	−3	−2	−2	−3	−4	−3
140	obs.	145	124	105	88	72	47	26	9	1
	obs.-calcd.	−16	−11	−7	−4	−4	−2	−2	−2	−2
180	obs.	113	97	83	70	58	37	19	3	−5
	obs.-calcd.	−25	−17	−11	−7	−3	0	1	1	0
220	obs.	81	72	63	54	45	29	13	−2	−11
	obs.-calcd.	−36	−24	−14	−8	−3	−4	5	4	2

The calculated values of μ for air (Table I) agree well with those derived from Roebuck's[4] data, except at the lowest temperatures, where there are reasons[2] to believe that the measured values may be in error. The average

deviation of the values calculated by use of the "approximate" relations (10) and (4) is 0.005, whereas Bridgeman[2] found that the average deviation resulting when the "complete" relations (2) and (3) are used is 0.0035.

TABLE II. *Comparison of the calculated with the observed values of the Joule-Thomson coefficient for ammonia.*

Calculations made with Equations (10) and (4).

In units of atmospheres, cm³ per gram and degrees Kelvin, the values of the constants for ammonia are $R=4.81824$, $A_0=3000$, $a=51.5$, $B_0=0.45$, $b=131$, $c=360\times10^6$.

Observed values are those of Osborne, Stimson, Sligh and Cragoe.

Temperature °C	Pressure meters of Hg	μ, °C per meter of Hg		Temperature °C	Pressure meters of Hg	μ, °C per meter of Hg	
		obs.	obs.-calc.			obs.	obs.-calc.
144.95	0.752	1.25	−0.03	30.15	1.527	3.39	.07
	2.323	1.24	−.01		1.532	3.47	.15
110.05	1.512	1.71	.06		1.760	3.42	.12
	10.411	1.70	.25		1.815	3.45	.16
70.05	1.513	2.41	.10		2.308	3.39	.15
52 50	1.303	2.70	−.02		2.326	3.58	.34
	1.518	2.82	.12		4.060	3.64	.58
	2.308	2.78	.14		7.110	3.58	.80
				−5.00	0.392	5.39	.37
					2.307	5.54	1.02
					2.478	5.47	.99
				−12.92	1.475	6.19	1.06
				−18.22	0.394	6.81	.98

The "approximate" equations (10) and (4) lead to values of μ for ammonia (Table II) which are in fair agreement with the experimental results above 30° but in poor agreement at the three lowest temperatures. The same remark[6] may be made concerning the values calculated by the "complete" equations (2) and (3) with the exception that the agreement is somewhat better throughout. The average deviation for all values at and above 30° C is 0.19 for the "approximate" equation and 0.08 for the "complete."

It is of interest to find out how well the "approximate" relation represents the inversion temperature of the Joule-Thomson effect. This is determined by placing $\mu C_p=0$, and from (10) we obtain

$$p=-\frac{-B_0+(2A_0/RT)+(4c/T^3)}{(2B_0b/RT)-(3A_0a/R^2T^2)+(5B_0c/RT^4)} \tag{11}$$

for the relation between the pressure and the inversion temperature. For zero pressure the inversion temperature can be obtained from the relation:

$$-B_0+\frac{2A_0}{RT}+\frac{4c}{RT^3}=0. \tag{12}$$

In Figure 1 is given a comparison of the calculated inversion temperature for air determined from (11) by use of the constants given in Table I with the values which Roebuck[4] derived from his measurements. Figure 1 is a reproduction of Figure 11 of Roebuck's paper with the curve determined by

(11) added. The curves of the inversion temperatures obtained by use of van der Waal's and Dieterici's equations are taken from Roebuck. Comparison of our Figure 1 with Figure 1 of Bridgeman's paper[2] which gives

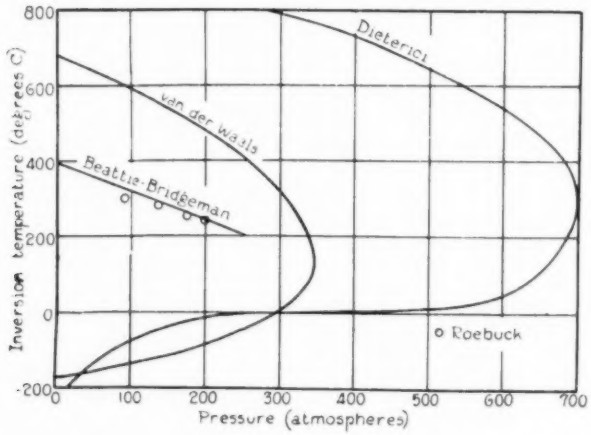

Fig. 1. Inversion temperatures of the Joule-Thomson effect in air.

the curve of the inversion temperatures derived from the "complete" equation shows that the values obtained from the "approximate" equation agree with Roebuck's points as well as those calculated from the "complete" equation.

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Atomic Oxygen as a Reducing Agent

The reducing action of hydrogen peroxide on certain metallic oxides is well known and the analagous reaction might be predicted for atomic oxygen. The authors have spent a considerable amount of time in this laboratory trying to obtain a reducing action by exposing various metallic oxides to a beam of oxygen atoms produced in the electrodeless discharge. No reaction was obtained except in the case of molybdenum trioxide where a reaction was obtained which appears to be identical with the reaction produced by atomic hydrogen. A target which has been covered with a finely divided deposit of molybdenum trioxide, which is light yellow in color, shows the characteristic slate blue trace where the oxygen beam impinges. Not only were traces of atomic hydrogen and atomic oxygen beams produced side by side on the same target, but beams of atomic hydrogen and atomic oxygen were impinged on the same spot in alternation. No change in the appearance of the blue discoloration could be observed on changing from the oxygen to the hydrogen beam, which seems to eliminate the possibility that the reaction with oxygen is the formation of a higher oxide.

Elaborate precautions were taken to free the oxygen from all impurities including water. In order to make certain of the active species the beam was passed through an inhomogeneous magnetic field. The central undeviated line characteristic of atomic oxygen (Phipps and Kurt, Phys. Rev. **34**, 1357, 1929) was readily obtained but no trace of side lines was observed. This is probably due to lack of intensity since the side lines should be fainter than the central line. It may be that the oxygen atom only reacts with the trioxide when it is in the $^2P_0$ state or it may be of course that the active species is not the atom but an activated molecule, the $^1\Sigma$ state for instance. It should be noted that the molybdenum trioxide is reduced only when it is separated by two slits from the discharge. If only one slit is used or the target is introduced into the discharge the blue coloration disappears almost instantly.

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W. A. NICHOLS, Jr.

Laboratory of Physical Chemistry,
University of Illinois,
March 5, 1930.

A Generalization of the Rydberg Formula

On the basis of the old quantum theory it was known that by carrying on a perturbation calculation one arrived successively at the Rydberg and then the Ritz formulas for the terms of a hydrogen-like atom. In the quantum mechanics it has been shown by Hartree (Proc. Camb. Phil. Soc. **24**, 1929) that for an atom with one electron in a central field a generalized Ritz formula holds at least for large values of N. This formula can be written (the series limit is here taken as the zero of frequency).

$$\nu_n = R/(n+\sum_0^\infty{}_i\, q_i \nu_n{}^i)^2. \qquad (1)$$

The ordinary Ritz formula is the approximation obtained when only the first two powers (0 and 1) of ν_n are used. To use more than two constants q_0 and q_1 would make the formula unwieldy and would scarcely help in the complicated cases while in the simpler cases additional constants are unnecessary. The two-constant formula of Ritz is however wholly inadequate to describe certain series of terms especially in the complex atoms.

If one follows the perturbation calculation of the quantum mechanics to two approximations admitting the possibility of more than one optical electron, one is led to suggest a substitute for the Ritz formula which has sometimes important advantages and in the other cases reduces to the Ritz expression. The theoretically derived energy equation can be put into the simple form:

$$\nu_n = R/\left[n+\sum_0^\infty{}_i\, p_{in}/(\nu_i-\nu_n)\right]^2. \qquad (2)$$

This form involves perhaps a slightly artificial but quite harmless definition of the term for which $i=n$—so that the first approximation (i.e. Rydberg correction) is taken into account without spoiling the appearance of the formula. For all other terms the ν_i are by no means arbitrary constants but are the observable spectroscopic terms. These as well as the properties of the p_{in} will be described in detail elsewhere. For the present only two remarks will be made.

I. In the most usual case there will be no term difference, ν_i with $p_{in}\neq 0$ small enough to be important. That is, all the terms in the sum can be expanded in powers of ν_n and the ordinary Ritz formula results if one uses only the first two terms in the expansion.

II. If there is more than one electron a possibility arises which has heretofore been left out of account. An electron configuration not belonging to a particular series may have an energy level for which $\nu_i-\nu_n$ changes sign with varying n while the corresponding p_{in}'s are not zero. The conditions for such a case are too complicated to be described in the present letter further than to say that they are stringent enough to explain why this case is not more common than it is found to be. In the neighborhood of such a ν_i the terms will be given by

$$\nu_n = R/\left[n+q_0+P/(\nu_i-\nu_n)\right]^2 \qquad (3)$$

and will show a remarkable irregularity which was first observed by Schrödinger (Ann. d. Physik **77,** 1925).

This case which arises, e.g. in Pb I, Ca I, Hg I, Al II, Si III, etc. is possibly the most common form of irregularity and in the past has invariably led to misidentification of terms. If one takes the theory into account and reassigns quantum numbers accordingly the applicability of Eq. (3) is obvious. The term ν_i is incidently located and because of the conditions on p_{in} is fairly definitely identified.

The chief contribution of this work is the satisfaction one gets from the elimination of an apparent flaw in our notions of line spectra. It permits a temporary relief from the feeling that our present theory is not complete enough.

R. M. LANGER

National Research Fellow,
University of Berlin,
February 14, 1930.

The Reflection of Hydrogen Atoms From Crystals of Lithium Fluoride

The work on the reflection of hydrogen atoms is now being extended to a study of the reflection from LiF crystals. These crystals were grown from the melt by a modification of the method of Ramsperger and Melvin. (Jour. Opt. Soc. **15,** 359, 1927). A freshly cleaved surface was mounted in the apparatus formerly used in the study of the reflection from NaCl and KCl, (Frank. Inst. **206,** 301, 1928), and bombarded with a sharply defined beam of hydrogen atoms issuing from a discharge tube.

Under favorable conditions the reflection in the specular beam from LiF was as high as 50% of the incident beam, as compared with 5% from NaCl, and 0.5% from KCl. As in the case of the other alkali halides which have been studied, the specularly reflected beam from LiF is confined to within the same angular breadth as the incident beam.

During the course of the investigation some peculiar fan-shaped patterns consisting of a central spot with radial streamers appeared on the molybdenum oxide coated detecting plate. Simultaneous with the appearance of these patterns the LiF crystal lost its atomic reflecting power and acquired a brownish tinge similar to what is usually observed on glass when bombarded by ions or electrons. If the copper crystal holder was maintained at +110 volts with respect to the surrounding case, these patterns disappeared. Furthermore, it was found that when the crystal holder was insulated similar patterns appeared on the plate even though the crystal was removed from the holder. It was therefore dem-

onstrated that these patterns were due merely to the electrostatic repulsion of the ions in the beam by the charge which accumulated on the crystal and the crystal holder. By applying an electric field across the beam to remove the ions, the fan-shaped patterns disappeared, the crystal remained clear, and its high reflecting power persisted for a long time.

With the discovery of this effect of ion bombardment on the reflecting power of LiF it became of interest to make a reinvestigation of the reflecting power of NaCl and KCl with the ions removed from the beam. The reflection from these crystals, however, appeared to be unaffected by the ion concentrations present.

The fact that the electrostatic charging of an insulated surface can deflect a beam of ions into irregular patterns, shows that one must be cautious in interpreting any pattern as the diffraction of de Broglie waves when ions or electrons are reflected from insulated crystals.

THOMAS H. JOHNSON
The Bartol Research Foundation,
February 19, 1930.

Multiple Coincidences of Geiger-Müller Tube-Counters

The ordinary method of coincidences [e.g. Bothe and Kolhörster, Zeits. f. Physik **56**, 751 (1929)] does not make possible the performance of experiments upon the individual very high energy β-particles which presumably give rise to the coincidences between Geiger-Müller tube-counters (*elektronenzahlröhre*), chiefly because suitable collimation by slits is nearly impossible in the interesting region of very high energies (10^8 to 10^9 volts) which this new instrument has opened to analytical experimental attack. It occurred to the writer some weeks ago that the observation of the coincidences between *three* tube-counters would make such a study possible. The first two counters would serve as a slit-system, defining a beam and "picking out" individual particles to be observed while the third movable counter would serve to detect these particles after being scattered, deflected by a magnetic field, or otherwise subjected to experimental conditions. Experiments are under way here for obtaining information on the probability of deflection of such extremely fast β-particles in various (small) angles in passing through a scattering block. The theory of multiple scattering indicates that the deflections may be below the practical limits of angular resolution, but even an upper limit, experimentally determined, for such extremely fast particles will be of interest. Other applications are readily devised.

This arrangement has another advantage which may be immediately appreciated—that of increased "resolving power" against accidental coincidences. If the resolving power of the means for determining coincidences between two tube-counters is such that say one out of 200 (residual) counts (a practical figure) in each individual tube-counter will be accidentally "coincident" within the specified range of resolution, the probability of such an accidental coincidence of *three* tube-counters within the same range of resolution is 1 out of 40,000. The idea of the *multiple*-coincidence method using a series of counters is an obvious extrapolation. Theoretically, any desired degree of freedom from accidental coincidence can readily be obtained, provided, of course, that the efficiency of counting is 100 per cent, as has been shown to be approximately true for β-particles. We do not yet have sufficient data to say how nearly true this is for the very fast particles with which we are dealing. Scattering deflections of the primary particle at the walls of the counters or in the air between counters will set an ultimate limit on the resolution which can be reached in practice even with perfect counting. Secondary effects may also be of importance. The actual resolving power will be less than that calculated on a probability basis also by reason of true coincidences produced only in part of the series of tube-counters by particles not capable of passing through the whole series. There is no doubt, however, that enormously increased resolving power can be obtained by the requirement of multiple instead of paired coincidences. The attainment of very great freedom from accidental coincidences is of greatest importance when it is desired to reduce the solid angle subtended by the tube-counters for true coincidences to a small figure, because of the large number of residual counts in comparison to those due to the very small intensity of the penetrating radiation. The possibility of using the multiple-coincidence method as the basis of a "gamma-ray tele-

scope" for exploring small areas of the sky is being investigated. The intensity of the penetrating radiation is very low for such a purpose if the definition of really small areas is desired unless, of course, later observations show the penetrating radiation to come from particular small areas of the sky rather than uniformly from all directions. An estimate hazarded on the basis of present data, assuming uniform intensity per unit solid angle, gives as the order of magnitude one true coincidence per 1,000 minutes for counters of cross-section 50 cm², subtending one square degree in the sky. Automatic recording of the amount of the penetrating radiation coming from particular areas of the sky, using two tube-counters and a special "coincidence circuit" somewhat similar to that recently published by Bothe [Zeits. f. Physik, **59**, 1 (1929)] was begun here early last November. The resolving power (for our circuit between 0.005 and 0.001 second) of such an arrangement without *multiple* coincidences constitutes a severe limitation on the smallness of the area which can be observed.

A few practical notes on a brief oscillographic study of the recovery-time of a tube-counter and associated amplifier-circuits under various conditions may be of interest to others who are using the instrument. The high resistances (5×10^9 ohms) used by Geiger and Müller and others require the tube-counter to operate at a variable voltage, since the time-constant of the circuit is even larger than the average time between counts, whereas lower resistances restrict the range of voltages which give satisfactory counting. By connecting the central wire of the tube-counter directly to the grid of the amplifier-tube, the recovery-time of the tube-counter may be observed. Oscillograms have been taken using this circuit with resistances from 1 to 5,000 megohms. The recovery-time increases rapidly as the voltage is raised above the minimum critical voltage at which counts begin (which is the same for all values of R), and varies by a factor of perhaps five for different single counts at any given voltage. The average recovery-time (to within five volts of the initial potential on the central wire) varies from perhaps 0.002 second at a voltage midway in the working range (of only a few volts) for $R=1$ megohm, to two seconds or more for $R=5{,}000$ megohms, where the true working range (actual voltage between central wire and tube) is considerably more than 100 volts. In spite of this very long recovery time of the tube-counter itself, however, a $0.00004\mu f$ blocking condenser between the tube-counter and the amplifier-grid, and a grid-resistance of 10 megohms, as used by Bothe, gives satisfactory counts on the first amplifier-tube up to several hundred per minute, and the recovery-time of this amplifier-tube is of the order of 0.001 second. The oscillograms using this arrangement show that of two counts 0.01 second apart the second one will be usually missed, but counts 0.1 second apart give ample impulses (UX201A tubes were used). These results could have been safely inferred, but perhaps some interest may be attached to their demonstration by oscillograms.

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February 24, 1930.

Temperature Shift of Spectral Lines and Pole Effect in Vacuum Arc

The work of many investigators has shown that the wave-length of most emission lines is a linear function of the total pressure acting when the vapor is in an arc, a furnace, or an absorption tube. It has been considered that the pressure shift per atmosphere is independent of the temperature. This implies that the experimental wave-length of a line from a source operating at constant pressure is independent of temperature. The chief purpose of this note is to report experimental evidence indicating that this view may be incorrect.

Two conclusions may be drawn from previous work: (1) that the wave-length of a line under given conditions of temperature and pressure is, at least for low values, independent of the partial pressure of the vapor, and (2) that ionic density plays a small part, if any, in the phenomenon of pressure shift. The first is justified by the conclusion of Babcock[1] that pressure shift is independent of changes in vapor density. The second may be justified by consideration of the results of King[2] and of Füchtbauer, Joos, and Dinkelacker.[3] King found a larger pressure shift per

[1] Babcock, Astrophys. J. **67**, 240 (1928).
[2] King, Astrophys. J. **35**, 183 (1912).
[3] Füchtbauer, Joos, and Dinkelacker, Ann. d. Physik **71**, 204 (1923).

atmosphere in the furnace than Babcock[1] found for the same iron lines in the arc. The value of the mean ratio for the pressure shift of lines common to the two lists is 2.3 with an average deviation of 0.3. The second paper reports pressure shifts for λ2537 of mercury in absorption at room temperature. These results indicate that molecular density, while not the ultimate cause, is probably the controlling factor in pressure shift.

An increase in pressure at constant temperature indicates an increased density of molecules. This change usually causes an increase in wave-length. A decrease in temperature at constant pressure might be expected to operate similarly.

The core of an iron arc of the Pfund type with cathode below is surrounded by a rather thick envelope of iron vapor and iron oxide dust. In an effort to establish the existence of a temperature shift a layer of this envelope was used by the author as a low temperature source of iron lines, while the central section of the arc with polarity reversed was used as a high temperature source. Two of the three lines selected for this test showed a shift in the direction indicated above, and of the right order of magnitude.

In order to check these results plates were taken of λ5890 of sodium. Shifts measured between four different types of sources gave results qualitatively in agreement with that indicated by the previous paragraph. It is considered that neither line asymmetry nor fine structure, as reported by Minkowski[4] and Schüler[5] respectively, can account for all the experimental data as easily as the hypothesis here suggested.

[4] Minkowski, Zeits. f. Physik **55,** 16 (1929).
[5] Schüler, Naturwiss. **16,** 512 (1928).

It therefore seems possible to measure, by means of this phenomenon, effective flame, arc, and furnace temperatures when the pressure is known. Assuming that the wavelength of a line is a linear function of the number of molecules per unit volume, that ionic fields of high value were absent from the sources of Babcock and King, and that the effective temperature of King's furnace was 2000°C, the calculated temperature of the effective emission point of Babcock's iron arc for the lines common to both lists is 5000°C ±700°C.

St. John and Babcock[6] found that a 6 mm iron arc was practically free from pole effect at pressures below 10 cm. However, an anomalous behavior of the yellow sodium lines has been reported by Kiess.[7] Both lines showed a shift of 0.004A between absorption in a low pressure tube and emission in a vacuum arc at 6 cm pressure. This indicates either that the pressure shift is non-linear at low pressures or that a positive pole effect existed in the arc used. Two sets of plates of λ5890 taken by the author showed a positive pole effect of 0.005A and 0.006A respectively in a carbon arc operated at about 10 cm pressure. Therefore it is suggested that care be used in applying this result of St. John and Babcock to any conditions other than those investigated by them.

All plates were taken at Yale University.

F. T. Holmes
Department of Physics,
Lehigh University,
Bethlehem, Pa.
February 26, 1930.

[6] St. John and Babcock, Astrophys. J. **42,** 231 (1915).
[7] Kiess, J.O.S.A. and R.S.I. **18,** 169 (1929).

Emission of Positive Ions From Thoriated Tungsten

In an earlier note, it was reported that tungsten when heated gave off positively charged tungsten ions. The emission from thoriated tungsten has been investigated and in addition to tungsten ions of mass 184, thorium ions of mass 232 and an ion of mass 247 ±2 have been obtained. This latter ion may be thorium monoxide, although all attempts to reduce it with H_2 have failed. It appears at an estimated temperature of about 2300°C. The alternative explanation is that it is some other extremely stable compound or an element. An x-ray investigation of various thorium sources is under way to settle this last possibility.

H. B. Wahlin
Laboratory of Physics,
University of Wisconsin,
February 28, 1930.

BOOK REVIEWS

Hydro-und Aeromechanik, Vol. 1. O. TIETJENS. Nach Vorlesungen von L. Prandtl. Pp. 238, figs. 178. Verlag von J. Springer, Berlin, 1929. Price RM 15.

This is a well-written introduction to the Hydro and Aerodynamics of inviscid fluids. The first section, which deals with topics that are of importance in aerostatics, is pleasing to the reader as it opens with brief sketches of the early work of Euler and Stevin on the pressure of fluids and then contains a particularly clear presentation of the statics of the atmosphere and the effect of different atmospheric conditions upon the behavior of a balloon. The section closes with an account of the phenomena of capillarity.

The second section is devoted to the kinematics of liquids and gases. It is pointed out that vortex-lines, stream-lines and paths of particles are not the only lines of kinematical importance because experiments in which foreign matter is introduced into the fluid at some point to render the motion visible have directed attention to the streak-lines (Streichlinien). A method of constructing streak-lines is explained and illustrated by means of diagrams. The section also contains a presentation of the geometry of vector fields and special attention is paid to the kinematical boundary conditions; in particular, the flow near the points of stagnation is discussed in an illuminating way and it is emphasized that liquids and gases are not ideal but only *quasi-continua*.

Section three deals with the dynamics of inviscid fluids and includes important applications of Bernoulli's Equation and Potential Motions. The chapters on vortex-motion and the influence of compressibility are particularly striking and should be of great help to the student who wishes to master the particularly fruitful methods by which Ludwig Prandtl has rejuvenated the science of Hydrodynamics.

H. BATEMAN

La Nouvelle Mecanique des Quanta. GEORGE BIRTWISTLE. Pp. vi+333. Paris, Librairie Scientifique Albert Blanchard, 1929.

This French translation of Birtwistle's book, "The New Quantum Mechanics" is hardly likely to be of much interest to American physicists. The English original[1] was a hasty compilation of the results of the new methods in atomic physics which was useful for reference in regard to formulas although it contributed scarcely anything toward a clear understanding of the theory. The French edition has four appendices by the translators, M. Ponte and Y. Rocard, amounting to 30 pages giving brief accounts of Dirac's relativistic electron theory, the revised electron theory of metals, fluctuations in the new statistics and the so-called "hydrodynamic" interpretation of wave mechanics.

E. U. CONDON

[1] Reviewed in Phys. Rev. **33**, 869 (1929).

The Terminology of Physical Science. DUANE ROLLER. Pp. 115, demy 8 vo. Paper cover. University of Oklahoma Press, 1929. Price $1.00.

Readers of text-books and research reports, and listeners to lectures and recitations are often irritated by non-conformity in the choice of words or in pronunciation. The booklet under review voices the irritation of one such reader and listener. The reviewer sympathizes with the author's state of mind but doubts the feasibility of his proposed reform by proclamation. The chance of success would be greater in this case if the author had not made blunders in etymology, shown little understanding of differences between synonyms, and used his non-scientific English inexpertly. The reader may also be shocked by the author's readiness to

recommend wide departures from standard usage and by his propensity for log-rolling in favor of his colleagues.

In spite of obvious faults of presentation the monograph should prove interesting and stimulating to members of that small group of physicists who wish to improve the intelligibility of their science. The fragmentary remarks on non-technical terms and on technical terms used in half a dozen other sciences are outside the scope of this review.

L. W. McKeehan

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE NEW YORK MEETING, FEBRUARY 21 AND 22, 1930

The 162nd regular meeting of the American Physical Society was held in New York City at the Physics Laboratories of Columbia University on Friday and Saturday, February 21 and 22, 1930. The presiding officers were Professor Henry G. Gale, President of the Society, Dr. W. F. G. Swann, Vice-President, Professor John Zeleny and Dr. Arthur E. Ruark.

The Saturday morning session was given over to a Symposium of Photoelectric and Thermionic Phenomena. The speakers were F. L. Mohler, F. K. Richtmyer, William V. Houston, C. E. Mendenhall and G. Wentzel. The titles of their papers appear in the following list of abstracts, numbered 46–50 inclusive. The symposium was attended by over 400 persons.

At the regular meeting of the Council held on Friday, February 21, 1930 twenty-two were elected to membership. *Elected to Membership*: Eugene C. Bingham, Kenneth C. Blanchard, Willard E. Bleick, Leo P. Delsasso, A. M. I. A. W. Durnford, Frank M. Exner, Charles F. Ffolliott, D. A. Fogelsanger, Omer R. Fouts, James D. Hardy, Mituyosi Igari, A. L. Johnson Jr., Wendell R. Koch, Richard H. Lee, William G. Moran, Yoshio Nishina, Luhr Overton, Elmer N. Turnquist, J. S. Webb, Herman G. Wehe, Donald B. Woodbridge and Oliver R. Wulf.

The regular scientific session consisted of 63 papers, Numbers 1, 2, 3, 8, 14, 15, 20, 32, 33, 42, 57 and 58 were read by title. The abstracts of these papers are given in the following pages. An **Author Index** will be found at the end.

W. L. SEVERINGHAUS
Secretary

ABSTRACTS

1. Transient earth currents accompanying the recent Newfoundland earthquake of 1929. RICHARD HAMER, *Acadia University.*—It does not seem to have been recorded hitherto that transient electric and magnetic disturbances were associated with earthquakes. It seems certain that such did accompany the recent earthquake off Newfoundland. Observations, similar or related, of others, besides personal, have been reported supporting the author's contention. The geophysical importance of such a fact is obvious. Several years ago the author proposed to account for variations of the earth's magnetic elements by assuming circulating earth currents. This granted, earth movements would obviously be accompanied by transient electron readjustments. However other possible causes exist; such as temporary readjustments of the electric activity of large mineral deposits and certain strata; also the possible frictional electricity generated due to the relative motion at the long break; and also polarization from fracture or piezoelectric effects on variations of stresses. By induction if not by conduction the temporary

influence of such electrical disturbances was transmitted with a speed approaching that of light in an expanding area around the epicenter. Ordinary seismic waves followed arriving later and later relatively at more distant regions. Thus the author determined the epicenter. The importance of studying earthquakes from this new angle is emphasized.

2. A modification of Wiechert's experiment. T. R. WILKINS AND J. A. WOOD, *University of Rochester.*—Wiechert's single equation method for a direct determination of the speeds of corpuscles has been modified by using a vacuum tube oscillator and an electrostatic deflecting field. This revives an experiment, theoretically very attractive but which has been experimentally extremely difficult. (See J. J. Thomson—Conduction of Electricity through gases.) Since the period of the oscillator can be held very constant, the difficulties experienced by earlier experimenters who used Tesla Coils and large high frequency currents to energize the deflecting fields disappear. The method would seem equally applicable to positive ray analysis or as a general corpuscular filter.

3. Polar molecules—their contribution to energy loss. F. HAMBURGER JR., *Johns Hopkins University, (Introduced by J. B. Whitehead).*—Some discussion has taken place during the last year as to the possible effects of molecular orientation as a source of dielectric loss. The suggestion has been offered that even at frequencies as low as those of commercial power circuits the theory of molecular orientation may be offered as an explanation of at least a portion of the dielectric loss. This paper is an attempt to examine this suggestion on the basis of the Debye theory and the available experimental data. It shows that in the case of glycerine at temperatures of zero and ten degrees Centigrade the loss due to orientation, at frequencies below ten thousand cycles per second, is negligible. Furthermore, it indicates that for the usual insulating oils, the possibility of accounting for even a portion of the dielectric loss observed at commercial frequencies, on the basis of molecular orientation, is remote.

4. Magnetoresistance and elastoresistance in permalloy. L. W. MCKEEHAN. *Yale University.*—A continuation of preliminary work reported by Arnold and McKeehan (Phys. Rev. [2] **23,** 114 (1924)). The effect of intensity of tensile stress upon the change in resistance due to magnetization has been observed in straight wires of annealed permalloy over a wide range in composition. Additional studies have been made on specimens containing 45, 77 and 84 percent nickel. In these latter wires the magnetization and resistance have been measured simultaneously. The resistance for a given magnetization is not single-valued, although a symmetrical "hysteresis" loop on the magnetization-resistance plane may cross itself. The magnetic fields were produced by long solenoids and the magnetic field intensity did not exceed 50 gauss in the definitive experiments. Under suitable conditions, however, this field intensity is sufficient for approximate saturation of the magnetoresistance effect. The results lend support to the view that adjacent atoms in a pure ferro-magnetic metal, and—*a fortiori*—in a ferromagnetic alloy, differ widely in those constraints which determine their dirigibility by externally applied forces.

5. Stabilized oscilloscope with amplified stabilization. FREDERICK BEDELL AND JACKSON G. KUHN, *Cornell University.*—One stage of amplification included in the stabilizing circuit of the Bedell-Reich oscilloscope, which comprises a cathode-ray tube with linear time-axis for observation of periodically varying quantities, extends the range of frequencies through which the curves on the screen of the cathode-ray tube may be stabilized and maintained stationary so that they can be photographed either with camera or contact print. Linearity of time-scale is shown by equality of successive wave-lengths and is controlled by an equalizing adjustment. Although not primarily intended for use beyond the audio range, the instrument has in this way been stabilized above 100,000 cycles. Curves are given showing the use of the instrument for the study of electrical quantities, as in the study of modulation and rectification, the ripple voltages in B-eliminators and filters and the wave-form of different oscillators; also curves obtained with photo-electric cell, showing flicker in candle-power in light sources, and curves, obtained with condenser microphone, showing wave-form of notes from musical instruments, the violin and clarinet. To be published in Review Scien. Instruments, April, 1930.

6. The initial stages of electrical breakdown. J. W. BEAMS AND J. C. STREET, *University of Virginia.*—A Kerr cell method (Beams, Jour. Franklin Inst. **206,** 809, (1929)), a simple comparison arrangement and a method making use of a rapidly rotating mirror (Beams, Phys. Rev. **33**, 1086 (A) (1929) have been used to determine the average time lag of the spark. The last method has also been used to photograph the different stages of the discharge. The time lag is decreased by ultra-violet light on the cathode, ions in the gap or by increasing the field strength. When a field of 4×10^4 volts/cm is very suddenly impressed, in ordinary air at atmospheric pressure containing the usual number of ions the average time lag is less than 5×10^{-8} sec. In dry filtered air, at atmospheric pressure, from which as many ions as possible were removed by auxiliary fields, 6×10^5 volts/cm could be applied for over 10^{-6} sec. without breakdown. Similar results were obtained with dry filtered hydrogen and nitrogen. Brass ball electrodes were used. The velocity of expansion of the spark is increased with decrease of pressure. At atmospheric pressure, the luminosity near the cathode becomes the most intense in approximately 2×10^{-7} sec. and gives rise to the well-known streamers. However at pressures roughly rom 0.008 mm to 0.001 mm the anode luminosity was found to be the most intense.

7. Some new types of electrical discharge in high vacua. R. W. WOOD, *Johns Hopkins University.*—Discharges excited in such high vacua as to be called non-conducting in the usual sense, excited through external electrodes with high frequency oscillators of wave-lengths varying from two to thirty meters. The effects of electric and magnetic fields upon the curious luminous balls and spindle shaped bodies (which have been named "plasmoids" provisionally) have been exhaustively studied, as well as the curious red phosphorescence of the glass which usually appears. Some progress has been made towards the explanation of these discharges by employing stroboscopic methods. The remarkable pressure changes which occur in the sealed off tubes as a result of "clean-up" or gas-evolution have been followed by vibrating quartz fiber mano-meters.

8. Complete dissociation of H_2. E. U. CONDON, *University of Minnesota.*—It is well known that where nuclear motions are involved mere energy sufficiency does not always make possible processes of excitation by electron impact or light absorption. Usually the critical potential in molecular hydrogen near 30 volts is interpreted as $H_2\rightarrow H^+ + H^+ +$ two electrons for which the energy needed is 4.4 + twice 13.5 = 31.4 volts. But this cannot be since if both electrons be removed the nuclei possess a mutual potential energy of about 18 volts. Therefore this process should require about 50 volts and when it occurs the protons formed would have kinetic energy of about 9 volts each. Just as Condon and Smyth (Proc. Nat. Acad. **14,** 871 (1928)) have interpreted the 11 volt dissociation as due to transitions from the normal state to the repulsive Heitler-London potential energy curve so now it is suggested that the loss at 30 volts is due to transitions from the normal state of H_2 to the repulsive Morse-Stueckelberg curve of H_2^+ in which case the process produces protons having about 6 volts of kinetic energy.

9. The primary ions formed by electron impact in hydrogen. WALKER BLEAKNEY AND JOHN T. TATE, *University of Minnesota.*—The results of a study of the primary products of ionization in hydrogen obtained with a mass spectrograph previously described (Phys. Rev. **34,** 157 (1929)) indicate that there are at least three different processes by which an ion may be formed by a single impact with an electron. (1) The molecular ion H_2^+ appears at 15.4 ± 0.1 volts as the result of the removal of one electron. (2) Ionization and dissociation occur simultaneously, yielding the atomic ion H^+ at a minimum potential of 18.0 ± 0.2 volts. (3) At about 30 volts another ion is formed, presumably H^+, which is characterized by the fact that it has several volts kinetic energy. It appears in the analyzer as a very broad peak and it also has been found to reach a side plate against the influence of a retarding field. The reactions (2) and (3) are much less probable than (1). These effects find a theoretical interpretation in the potential energy curves of Morse and Stueckelberg for the hydrogen molecule, as Condon has pointed out in the preceding paper.

10. The reflection of hydrogen Atoms from crystals of lithium fluoride. THOMAS H. JOHNSON, *The Bartol Research Foundation.*—The reflection of hydrogen atoms from crystals

studied at first with NaCl and KCl crystals is now being extended to other alkali halides. The preliminary results with lithium fluoride are interesting in two respects. In the first place a sharply defined specular beam appeared as with the other alkali halides heretofore tried but LiF may, under favorable conditions, reflect up to about fifty percent of the incident beam in the specular direction as compared with 5 percent for NaCl and 0.5 percent for KCl. In the second place it has been found that the reflecting power of LiF is strongly affected by the action of the atomic hydrogen or other products of the discharge tube which is used as the source of the atomic beam. Thus it has been found that a crystal at room temperature, though exposed to atmospheric air and to the molecular hydrogen from the unexcited discharge tube for some time, reflected the atomic beam intensely at first but the reflection had fallen off to one half of its initial intensity in a time of the order of one minute. At higher temperatures the same fatigue occurred but the reflection persisted for longer times up to about an hour.

11. Molecular beams in electromagnetic fields. D. E. OLSHEVSKY, *Yale University.*—A systematic synthetic study of possible arrangements of the vector quantities characteristic of a molecular beam experiment such as field strength, field gradient, molecular moment, velocity of beam and force is made. Known experimental arrangements of Kallman-Reiche, Stern-Gerlach, Rabi and of Clark are thus classified and their features clearly brought out. Analysis yields several new experimental arrangements of interest. Briefly, they are: (a) Reversal of beam direction in Rabi's experiment, the last slit being in the magnetic field and beam coming *out* of the field, with expected improvement in resolution; (b) Arrangement of field gradient at right angles to field and beam direction with possibility of detecting molecules oriented perpendicular to field; (c) Arrangement with the second slit consisting of two closely spaced, field producing wedges, the beam perpendicularly to the plane of the slit. Arrangement (c) seems to be particularly efficient due to the fact that the beam can be left larger than slit spacing, the second slit serving as a highly efficient microscopical field-producing unit.

12. Recombination of hydrogen-like atoms. E. C. G. STUECKELBERG AND PHILIP M. MORSE, *Princeton University.*—The probability that an electron moving with a velocity of V volts recombines with a hydrogen ion or with an ion having a similar field and resultant nuclear charge Ze to form an atom in a state defined by the quantum numbers n, l is usually expressed by the effective cross section of recombination $q(n, l, Z, V)$ cm^2. The transition probabilities have been calculated from the matrix elements referring to the two states. A solution of the Schroedinger equation in a Coulomb field giving at large distances a plane wave has been found by Mott and by Temple. With the aid of this function an exact expression for the q's has been obtained, which decreases monotonicly with increasing V. For V small compared to $-E_{n,l}$ (the term value) an asymptotic formula can be used of the form $q(n, l, Z, V) = 1.237 \times 10^{-19} \cdot e^{-4n} \cdot C_{n,l}, Z^2/V$. The values for $C_{n,l}$ have been computed for $l=0$ and $n=1$, 2 and 3; for $l=1$ and $n=2$ and 3. $C_{n,l} \cdot e^{-4n}$ decreases for increasing n and approaches 0 for $n=\infty$. For some of the states the exact expressions for any V have been computed. They show in order of magnitude as well as in functional behavior a fair agreement with the older theories and the experiment. However, this theory can not explain the experiments by Barnes and Davis and it seems that their results must be due to a more complex reaction than simple recombination.

13. A search for critical potentials for electron recombination with Hg^+. A. M. CRAVATH, (*National Research Fellow*), *Princeton University.*—The discovery by Davis and Barnes (Phys. Rev. **34,** 152 (1929)) that electrons which have just enough energy to ionize He^+ recombine astonishingly rapidly with He^{++} suggested a search for recombination of 10.4 volt electrons with Hg^+. A cylindrical ring electrode 0.6 cm long, 2.5 cm diameter, was placed in a large Hg vapor arc, pressure 0.01 mm, ions per cm^3 up to 1.5×10^{11}. Electrons from a small oxide coated filament along the axis of the cylinder were accelerated in the thin sheath around the filament and then travelled out radially through the nearly equipotential ionized vapor to the cylinder whose potential was positive to the filament but negative to the space. The effect sought was a sharp reduction in the electron current reaching the cylinder when the electron energy passed through 10.4 volts. No effect was found. This may be due to the narrow-

ness to the range of energies for which recombination has a high probability, only a fraction of the electrons in the stream from the filament ($T \sim 1000°K$) having energies in this range. If this range had been comparable in width to the peaks in Davis and Barnes' experimental curves practically the whole electron stream would have been stopped.

14. Sorting the variables in the crystal structures of certain chromium-nickel alloys. F. C. BLAKE AND JAMES O. LORD, *Ohio State University.*—Microphotographs of certain chromium nickel alloys containing from 63 to 85 percent chromium revealed three phases present. The melts were made in a partial vacuum in crucible of alumina and were practically free from carbon. It was noted in general that after the power for the furnace was shut off but the partial vacuum maintained that the vacuum increased showing that some of the residual gases were being absorbed by the melt. Examination revealed nitrogen present in the melt. One phase was readily found to be body-centered chromium. Further experimentation revealed another phase to be chromium nitride and by the use of proper etching reagents a third phase was found to be chromium nickelide, Cr_2Ni, with ninety-six atoms to the unit cell, the cell consisting of four interpenetrating lattices of nickel with four other interpenetrating lattices of chromium, the lattice being body-centered tetragonal with $a = 10.64$A and with an axial ratio of 1.040. The density of the tetragonal phase is identical with that of body-centered chromium, *viz.* 6.93. Both the nickelide and the nitride are very hard and practically insoluble in hot aqua regia, especially the nitride. The lattice of chromium nitride was proved to be close-packed hexagonal with $a = 2.751$A., the axial ratio being 1.605, the unit cell consisting of two atoms of chromium and two of nitrogen. This gives a calculated density for chromium nitride of 7.75. The space group for the nitride is D_3^2 with the two nitrogen atoms interpenetrating. The possibility of a fourth phase being present is discussed.

15. An interesting case of a unit lattice made up of interpenetrating lattices. F. C. BLAKE, *Ohio State University.*—Some of the most interesting and important cases of alloys and solid solutions can be studied only by the powder method, for with several phases present no method has yet been devised for obtaining large single crystals of the phases separately. Indeed the importance of many of the alloys industrially is due to the very fact that their crystallinity consists only of *micro*crystals. Thus the powder method is the only one available. After considerable effort spent more or less uselessly trying to guess at the structure of a tetragonal chromium nickelide a deliberate attempt was made to see if one could build up synthetically a series of interpenetrating lattices of chromium and nickel which would give the reflection intensities observed. This was found to be possible, the lattice consisting of thirty-two atoms of nickel and sixty-four of chromium and having the property of unusual hardness spoken of by Professor W. H. Bragg (Proc. Royal Inst. **XXVI,** 6 (1929)) for many-atomed lattices of alloys of copper with aluminum, zinc and tin. The most interesting property of such a lattice is that the first sixteen lines that one might expect to be strong on the powder photograph do not appear at all, in agreement with observation. The space-group of the lattice found is D^{10}_4, a hemihedral form.

16. The classes of symmetry possible in crystals of elements. R. H. CANFIELD, *Naval Research Laboratory, Anacostia, D. C.* The object of this study is to determine the types of space-lattices possible in crystals composed of atoms of one kind and subject only to mutual central forces, the force between two atoms being zero for only one value of the distance. It is found that the conditions of equilibrium of one atom require that the center of gravity of any group of atoms which lie on the surface of a sphere shall lie at the center of the sphere. This condition of what may be termed "barycentric symmetry" limits the possibilities to 21 out of the 32 recognized classes of symmetry. Equilibrium against a generalized infinitesimal strain of the whole crystal imposes the condition that the principal axes of inertia of all such spherical groups of atoms shall have the same directions, and the principal moments of inertia be in the same proportion. This limits the possible classes still further to the five classes of the cubic system. It is concluded that since there are many exceptions to the latter rule many crystals even of elements cannot be regarded as homopolar in the sense of the first paragraph.

17. Excitation potential of the $L\alpha$ satellites of Ag (47). S. W. BARNES AND F. K. RICHTMYER, *Cornell University.* A precise knowledge of the excitation potentials of satellites should make it possible to distinguish between the Wentzel-Druyvesteyn theory of their origin and the so-called "two-electron jump" theory proposed by one of the present authors. The very meagre data in existence indicate that the excitation potentials of satellites are of the order of 20–40 percent higher than those of the corresponding parent lines. Using a Siegbahn vacuum spectrograph and a transformer-kenotron-inductance voltage supply which gave a ripple of much less than one percent, a series of exposures were made at 7, 6, 5, 4.5 and 4.4 kilovolts, respectively, on the $L\alpha$ line of Ag(47), the excitation potential of which is 3.35 k.v. Satellites were clearly visible on the plates taken at 4.5 k.v. and higher, but were not visible on the plate taken at 4.4 k.v., although the intensity of the parent line on the 4.4 k.v. plate was greater than on that at 4.5 k.v. However, the $L\alpha$ line at 3.8 k.v. shows an unsymmetrical "foot", which may indicate the presence of an unresolved satellite structure. If so, the excitation potential of the satellites may be much lower than 4.4 k.v. Acknowledgment is made of assistance from the Heckscher Research Council of Cornell University.

18. Satellites of $K\alpha$ for the elements Ni(28) to As(33). F. K. RICHTMYER AND E. RAMBERG, *Cornell University.*—The satellites $K\alpha_{3,4}$ of the line $K\alpha$ have been recorded previously from Na(11) to Zn(30) at which point they seemed to disappear. At Zn(30) the N shell begins to grow, which fact, it was previously thought, might be in some way related to the disappearance of the satellites. However, exposures made to bring out the satellite structure of the $K\alpha$ line of the elements Ni(28) to As(33) show that satellites (unresolved on the photographic plate) are clearly visible up to As(33), although they are relatively much less intense than for elements of lower atomic number. Observations by means of the two-crystal spectrometer show that the satellites $K\alpha_{3,4}$ of Cu(29) are clearly resolved into the two components, as is found by the photographic method for lower atomic numbers. These new data fit the Moseley type of graph for satellites proposed by one of the authors (F. K. R., Phil. Mag. **6**, 76 (1928)). Acknowledgment is made of assistance from the Heckscher Research Council of Cornell University.

19. Position and width of the modified line of the spectrum of scattered x-rays. F. L. NUTTING, *The Drexel Institute, Philadelphia.*—The Compton Shift $\delta\lambda = h/mc(1-\cos\phi)$ was tested at definite, large scattering angles by two independent methods. (a) *Photographic method.* Using fluorescence radiation before and after for fiducial marks, Mo radiation was scattered at 169 degrees from paraffin for 300 hours (maximum spread of scattering angle 12.5 degrees). The mean value of the shift of the center of gravity of the $K_{\beta\gamma}$ line on microphotometric curves gave $h/mc = 0.0231\text{A} \pm 0.00023\text{A}$. The shift of the peak of the β line (corrected for the presence of the γ line of 1/7.7 its intensity) gave $h/mc = 0.02376\text{A} \pm 0.00023\text{A}$. (b) *Ionization method.* Using two narrow cylindrical Mo tubes side by side and a Soller slit to increase intensity and scattering at 170 degrees from graphite (maximum spread of scattering angle 8 degrees), the mean of a large number of runs gave $h/mc = 0.0240\text{A} \pm 0.00024\text{A}$ for the shift of the K_α doublet. *Components.* No definite evidence of components appeared in the mean microphotometric curve, although the fluorescence α doublet was clearly resolved and the angular spread of scattering small.

20. The quantitative application of the irregular doublet law to an isoelectronic sequence. R. A. SAWYER, *University of Michigan,* AND J. E. MACK, *National Research Fellow, University of Minnesota.*—Heretofore the irregular doublet law of x-ray spectroscopy has been applied in isoelectronic sequences only qualitatively. (i.e. $\nu(n, l_1) - \nu(n, l_2)$ is a linear function of Z). Now Wentzel's result $\sigma_1(n, l+1) - \sigma_1(n, l) = 0.58 \cdot 2^l n$ for the first order screening number σ_1 in x-rays is applied, determining the rate of dependence of the energy of the transition $2s^2 2p^5 \leftarrow 2s 2p^6$ upon the atomic number Z in the fluorine-like sequence, to be $49 \cdot 10^3\ \text{cm}^{-1}$. New experimental results in Na III and Mg IV show it to be $48.01 \cdot 10^3\ \text{cm}^{-1}$. Although such accurate predictions are not generally possible for an arbitrary number of electrons, certain regularities may be used for interpolation in many cases.

21. The quantum theory of x-ray exposures on photographic emulsions. A. P. H. Trivelli, *Eastman Kodak Co.* (*Introduced by L. A. Jones.*)—The quantum theory of photographic exposures as proposed in 1922 by L. Silberstein had to be given up on account of the fact that the differences in sensitivity of the grains are determined not only by the projective area of the grain; a chemical factor is also entering into it for visible radiation. Kinoshita and Th. Svedberg have showed that every α-particle hitting a silver halide grain makes it developable. The sensitivity of the grain is, therefore, determined by its projective area and the probability that a grain is made developable by exposure to α-particles is given accurately by the equation, $p = 1 - e^{-na}$ (a = projective area, n = number of α-partjcles). An investigation with L. Silberstein has shown that the same equation holds for x-ray exposures.

22. A theoretical and experimental study of the resonance radiometer. J. D. Hardy, *Johns Hopkins University.* (*Introduced by A. H. Pfund.*) The voltage sensitivity limit of steady deflection galvanometers, regardless of degree of magnification or precision of manipulation, has been shown to be of the order of 10^{-9} volts. This is the natural sensitivity limit set by the Brownian fluctuations in the suspended system causing a random zero unsteadiness The calculation has been made for the case of the resonance radiometer (See Abstract of A. H. Pfund, Science Feb. 1929) and the results show that this natural limit has been lowered by about one hundred times, that is, to the order of 10^{-11} volts, in the present apparatus with a possibility of still further lowering the limit by mechanical and electrical improvements. Some results are given to show that without much precaution a sensitivity surpassing that heretofore obtainable can be realized and one that is very close to the theoretical limiting value. The smallest energy difference that has been with certainty distinguished is of the order of 10^{-4} ergs per second per square millimeter. A method is described for measuring the speed of response of thermocouples. The average speed of the thermocouples used was found to be 0.2 sec. in air and 2 minutes in vacuum.

23. High dispersion in the infra-red. R. Bowling Barnes, *Johns Hopkins University.*—For the purpose of comparing the Raman effect with infra-red absorption spectra, the following organic liquids have been measured from 3.1μ to 3.6μ: benzene, toluene, ortho-, meta- and para xylene, ethyl-, butyl-, monochlor-, and monobrombenzene. The spectrometer employed an echelette grating, which had 3600 lines per inch, and which concentrated the energy of a Nernst filament into the region which was investigated. The dispersion of the instrument was such that with the slits each 0.25 mm in width, one "slit width" was approximately 25A". The calibration was obtained in terms of the positions of the 5461 line from an auxiliary Hg arc, and the wave-lengths as given are considered accurate to $\pm 0.003\mu$. In every case the bands in this region, due to the C-H vibration, which have hitherto been reported only under low dispersion have been resolved into many component parts. The 3.25μ band of benzene was resolved into three equally strong components lying at 3.231, 3.253 and 3.291μ respectively. The shifts of these bands caused by the various substitutions were studied, and in no case was a shift of over 0.01μ found. Published data on the Raman effect failed to reveal the complexity shown by these absorption spectra.

24. Iodine fluorescence in the infra-red. F. W. Loomis, *University of Illinois.*—Oldenberg has photographed in the infra-red the fluorescence spectrum of iodine excited by the mercury arc. The spectrum is chiefly an extension of the well-known series of doublets excited by the green mercury line; but in the neighborhood of the infra-red doublets there appear other lines. Pringsheim attributes these to transitions to the extraordinary new molecular level which he reported. It is now found, however, that they disappear when the yellow lines are filtered from the light of the mercury arc. They should therefore be attributed to the higher members of the fluorescence series excited by the yellow lines. The relatively high intensities of these members is due to their being on the right arm of the Franck-Condon parabola.

25. The relation between Raman spectra and the molecular structure of organic compounds. Donald H. Andrews, *The Johns Hopkins University.*—The following procedure is

proposed for identifying the type of vibration in the molecule to which an observed frequency in a Raman spectrum corresponds. It is assumed that the only forces acting between the atoms in the molecule are those produced by the chemical bonds, and that there is a restoring force if the bond is stretched or if the angle which the bond makes with the other bonds on an atom is altered from the normal equilibrium value. It is also assumed that all non-polar chemical bonds have the same force constants. The different frequencies observed in the Raman spectra may then be considered as due solely to the variation in mass of the atoms concerned and to their space relation to each other, that is, whether they are in a straight chain, a branching chain, a ring, etc. It is possible to calculate in this way the number of Raman lines which should be observed for any compound, and the frequencies they should have. There is fair agreement with the observed spectra, close enough so that the lines can be identified with different types of motion in the molecule, and calculations of specific heat can be made.

26. A theory of zodiacal light. E. O. HULBURT, *Naval Research Laboratory.*—Since solar outbursts which give rise to aurorae and magnetic storms also cause changes in the zodiacal light it is possible that the zodiacal light is mainly sunlight re-emitted by the absorbing particles and not scattered or reflected by them. This permits a reconsideration of an old view that the particles originate in the earth's atmosphere, although the 15 percent polarization of the zodiacal light is left unexplained. Neutral atoms and molecules of the upper fringe of the earth's daytime atmosphere upon collisions of the second kind are ejected upward with velocities around 11 km sec^{-1} to 30,000 or 80,000 km levels where they are ionized by the solar ultraviolet light. Under the action of gravitation, the earth's magnetic field and the pressure of solar radiation, an oblong ring of ions and electrons is formed around the earth in the plane of the ecliptic, the ion densities being fairly low, below 10^3 cm^{-3}; this gives rise to the zodiacal light. The ring is perhaps 50,000 km distant on the daylight side of the earth. On the night side the ring stretches out to great distances 10^5 or 10^6 km. At its far end ions continually stream away in the direction of the sun's rays, so that the ring merges into a sort of comet's tail which may be the Gegenschein. Quantitative estimates are made throughout which depend on apparently acceptable assumptions of light pressure, time of ionization, etc. The estimates suggest a rate of escape of the earth's atmosphere of perhaps 10^6 ions cm^{-2} sec^{-1}, or about 10^{-6} of the atmosphere in 10^6 years.

27. A recording interferometer. C. W. CHAMBERLAIN, *Michigan State College.*—Light from a broad slit, illuminated by an incandescent filament, is collimated and divided into two parts which travel separate paths, one variable in length. The beams are reunited, with their wave fronts parallel, passed through a Wadsworth or constant deviation prism, and viewed through a telescope focussed for infinity. With eyepiece removed circular Fizeau fringes are seen in monochromatic light, when the interfering paths are unequal. With the eyepiece in position, a new type of interference system in white light is brought into view. The continuous spectrum is crossed by sharp dark bands whose positions in the spectrum correspond with the wave-lengths for which the interference system is opaque, or the path difference is an odd number of half wave-lengths. The number of bands appearing in an octave is identical with the path difference of the interfering beams, measured in terms of the longest wave. Lines appearing in that portion of the spectrum between 5016 and 6678 of helium correspond to a linear movement of one ten thousandth of a centimeter. In a similar manner, a range of spectrum may be arranged such that a change of one line in the range corresponds to a movement of five hundred-thousandths of an inch or any desired decimal part of an inch or centimeter.

28. An interference method of measuring distance. STUART H. CHAMBERLAIN, *Michigan State College.* (*Introduced by C. W. Chamberlain.*)—A collimated beam of white light is divided into two parts, slightly separated and converging toward a mirror, at a distance to be determined. The returning beams, slightly diverging, are received by an interference system which renders them parallel and permits lateral and linear displacements of the parallel wave fronts. The beams are passed through a prism and viewed through a telescope focussed for infinity. A dual system of interference bands is formed; one serviceable for accurately adjusting the

instrument to receive the returning beams, the other to measure the distance between the light source and the distant mirror. The distance is determined by the number of dark bands appearing in a continuous spectrum. The new method substitutes a portable base line measured in wave-lengths of light and an interference method of determining the angle subtended by this base line at the distant mirror for the present method of measuring by means of angles and a fixed base line.

29. On the question of aberration of the light from terrestrial sources and its application to the experiment of Esclangon. N. GALLI-SHOHAT, *Mount Holyoke College.*—The definition of the "relative" ray in the classical ether-theory is usually given by means of two small openings through which light passes. The question is how to direct the moving telescope (two openings) —one system— in order to observe the light traveling along a wave normal in the other system (ether). A more careful analysis of this definition from the standpoint of the cinematics of the question gives the result that the direction of the ray actually observed depends upon the orientation in space, the angle x representing *the aberration of light from terrestrial sources* being $\beta^2/2 \sin 2\theta_0$, $[\beta^2 = (v^2/c^2),\ \theta_0 = (l_0, v)]$. This method of construction of the relative ray when applied to the experiment of Esclangon gives a satisfactory explanation of the effect observed. The curve calculated for this case, using for the declination of the apex δ 68°, coincides with that given by Esclangon and the values of the right ascension, α and the velocity v of the apex came out as $\alpha = 20^h$ and $v = 200$ km/sec in agreement with modern astronomical data. This second order aberration should also give account for anomalies observed by astronomers and may change the theory of the Michelson-Morley-Miller experiment.

30. Resonance and quenching of the third principal series line of caesium. C. BOECKNER, *Bureau of Standards, Washington D. C.*—A helium discharge is used as a source for the study of the resonance radiation from the third principal series line of caesium. This is possible, due to the coincidence of a strong helium line with the caesium line. In addition to the resonance line, a number of caesium arc lines are observed. These have their origin in lower levels populated by radiation transfers from the initial $4\ P_{1/2}$ level. The effect of helium on the fluorescence radiation is studied. It is found that collisions between helium atoms and caesium atoms in the $4\ P_{1/2}$ state transfers the latter only to states differing by less than several hundredths of a volt from the initial state. This type of transfer occurs at approximately every kinetic theory collision. Transfers to states differing by as much as 0.18 volts are improbable.

31. The effect of gases on ionization of caesium by line absorption. F. L. MOHLER AND C. BOECKNER. *Bureau of Standards, Washington.*—Measurements consisted of obtaining sensitivity curves for a space charge tube containing caesium at a constant partial pressure when various foreign gases were put in the tube. Hydrogen and nitrogen at pressures of one or two cm reduce the ionization by line absorption to nearly zero. With helium and argon the effects at the fourth and higher lines approach at high pressure values ranging from 60 to 90 percent of the vacuum value but helium increases the effect of the third line. From data on the effects at different pressures we obtain values for the product of the lives of the excited states of caesium and the effective collision areas. This product remains of the same magnitude for different gases and for different excited states.

32. The spectrum of doubly-ionized antimony. R. J. LANG, *University of Alberta.*—The spectrum of the 49 electron atom of antimony consists of term of even multiplicity of which twenty-six have been found as follows: $(s^2 5p)^2P$, $(s^2 6p)^2P$, $(s^2 4f)^2F$, $(s^2 5f)^2F$, $(5p^3)^4S$, $(s 5p^2)^4P\ ^2D\ ^2S\ ^2P$, $(s^2 5d)^2D$, $(s^2 6d)^2D$, $(s^2 6s)^2S$, $(s^2 7s)^2S$, $(s^2 8s)^2S$, $(s^2 5g)^2G$, $(s^2 6g)^2G$. The ionization potential corresponding to the approximate value of the deepest term $(s^2 5p)^2P_1 = 200\ 272$ is 24.72 volts. In Sn II the $(s\ 5p^2)^4P^2S$ terms are located and also the $(s\ 5p^2)^2S$ in In I.

33. Nuclear spin and hyperfine structure. H. E. WHITE, *Physikalisch-Technische Reichsanstalt, Berlin, Germany.*—It appears that when hyperfine structure is to be attributed to nuclear angular momentum or spin i, that the relation $\Delta\nu_g : \Delta\nu_f = m_k : 4im_s$, should approximately

hold where $\Delta\nu_g$ is the gross or multiplet structure separation, $\Delta\nu_f$ the hyperfine structure separation, m_k the mass of nucleus and m_e the mass of electron. From a discussion with Dr. Schüler it appears that the hyperfine structure of λ5486 in Li II (Zeits. f. Physik **42,** 487 (1927) $^3S_1-{}^3P_{0,1,2}$, may be accounted for by assigning an angular momentum $i=\frac{1}{2}$ to the nucleus of Li^7. From the observed hyperfine structure the $^3S_1(1s2s)$ term and the $^3P_2(1s2p)$ term have normal doublet separations of about 0.60 cm^{-1}, and 0.45 cm^{-1} respectively. From the already known relations in hyperfine structure, the $^1P_1(1s2p)$ term should have an inverted doublet separation of about 0.40 cm^{-1}. The gross-structure difference, $^3P_2-{}^1P_1$, 5700 cm^{-1} as compared with the hyperfine structure difference $\sim$0.85 cm^{-1} gives a ratio of 6700 in good agreement with the theoretical value 6440. Equally as good agreement between theoretical and observed values is found in several other elements. A more detailed explanation will be given in the Physical Reviews.

34. Average lives of lines of mercury triplet 2^3P-2^3S. R. H. Randall and Harold W. Webb, *Columbia University.*—The average life of each of the three components of the mercury triplet $2^3P_{012}-2^3S_1$, when excited by electron impact under conditions involving negligible ionization has been measured. The method used was that previously described (H. W. Webb, Phys. Rev. **24,** 113 (1924)), in which high frequency voltages are applied in phase to the excitation and detecting systems. From the variation of the current with frequency the rate of decay of the radiation after the exciting impact is calculated. The lines were excited in a sealed-off tube with mercury pressures between 0.004 and 0.03 mm. The exciting voltage was less than ten volts. The excitation was such that there was no appreciable concentration in the excited 2^3P states. A specially designed potassium hydride photoelectric cell was used as the detecting system. Optical filters were used to isolate the line under measurement. The results agree with the assumption that the radiation decays exponentially after impact. For the lines λ4047 and λ4358 the lives were found to be the same within the experimental error (0.75%), viz. $\tau=5.75\times10^{-8}$ sec. The value for λ5461 was four times greater, $\tau=2.37\times10^{-7}$ sec. No satisfactory explanation of these results has been found. It is suggested that the fine structure of the lines may be involved.

35. The comet tail bands of carbon monoxide. Louis R. Maxwell, *Research Fellow, Bartol Research Foundation.*—The experimental arrangement described by the writer (Phys. Rev. **32,** 715 (1928)) for measuring the life in the excited states, can be used for determining whether the emitters of band spectra are positive or negative ions or neutral molecules. This method is now applied to the comet tail bands which were produced by impurities in the tube containing helium when excited by 140 volt electrons. The bands experienced a displacement along their length by such an amount as to show clearly that they are produced by positive ions. This confirms the conclusions which have been made in regard to their origin.—By decreasing the pressure to less than 1×10^{-4} mm these bands appeared strongly without the presence of other bands and with the helium spectrum extremely weak. By circulating helium through the tube at 1×10^{-3} mm both spectra were obtainable while further increase of the helium pressure lessened the intensity of the bands until at 2.8×10^{-3} mm they had practically disappeared leaving only the helium spectrum. This effect is opposite in character to the phenomena found by Merton and Barrett and others where small traces of CO in helium at 20 to 60 mm were capable of producing the comet tail bands quite brilliantly.—Since the positions of the bands are altered by the cross-electric field, it is possible to measure their mean life by the method previously used for the mercury spark spectrum.

36. The application of least squares. W. Edwards Deming, *Bureau of Chemistry and Soils, Washington, D. C.*—By writing general relations between the most probable values of observed quantities and of p parameters, it is possible to get a solution to the general problem. The different relations that may exist between the most probable values and the parameters constitute the distinctions between the various types of problems. The general solution takes the form of symmetrical equations. When $p=0$, it reduces to the so-called "method of correlates." For curve fitting, the general solution can be transformed into two sets of equations;

one gives the parameters, the other corrects the observations. Provision is made for cases where the empirical surface must pass through given points. Heretofore it has been customary to throw all the adjustment on to one group of observations and none on to the others—a practice that often contravenes the foundation of least squares and yields unreasonable results, resulting in unjustified criticism of the principle. The present method allows the proper weight of each observation to be used in the adjustment. The corrections give interesting geometrical generalizations of those discussed by the writer in the Proceedings of the London Physical Society for February 15, 1930.

37. Simultaneous irreversible processes. L. ONSAGER, *Brown University.*—A general theorem applying to simultaneous irreversible processes is derived from the assumption that the dynamical laws are symmetrical with regard to past and future. The derivation involves the consideration of fluctuations. The adaptation to processes obeying linear differential equations of the first (or second) order with regard to the time yields an extension of Lord Rayleigh's "principle of the least dissipation of energy." This result provides a satisfactory basis for certain theorems which were originally derived from the consideration of cycles differing from those accepted in thermodynamics in the essential respect that reversible operation is impossible. One of these theorems applies to thermoelectric phenomena (W. Thomson), another to liquid junction potentials in electrolytes (H. v. Helmholtz), a third one to the Soret effect (E. D. Eastman). A new theorem applying to diffusion is also obtained. An external magnetic field disturbs the straight symmetry in past and future (a rotating frame of reference has the same effect). In such cases another symmetry condition connected with a simultaneous reversal of the time and the magnetic field is applicable. On this basis a relation between the Nernst and the Ettingshausen effects, first proposed by P. W. Bridgman and H. A. Lorentz, is confirmed.

38. Thermodynamics of systems with several equilibria. N. RASHEVSKY, *Westinghouse E. and M. Co., East Pittsburgh.*—Further studies on thermodynamical systems having more than one equilibrium constitution for given external conditions, and discussed in a paper presented at the last February meeting, are made. A reversible reaction between two substances which are either dissolved or gaseous, but which in either case are following not the ideal gas laws, but van der Waals' equation, is considered. It is shown that for certain values of temperature, total volume and other external conditions; the free energy of the system, considered as a function of the ratio of the two reacting substances, has *two* minima. Hence, for given external conditions, the system may have two equilibrium concentrations. In other words, the state of the system is not defined by the external conditions alone, but, as has been shown in a previous paper, it depends also on the previous history of the system. We may say that the system possesses hysteresis. Different possible kinds of such a hysteresis and possible application, especially to some biological problems, are discussed.

39. An acoustical analogy of the Schrödinger wave equation. R. B. LINDSAY, *Yale University.*—Investigation is made of the one-dimensional compressional vibrations of an ideal fluid of variable density (in equilibrium under the action of an external force) confined in an infinite tube of bounded but variable cross section. The non-homogeneity is so chosen that the wave velocity is everywhere the same. It is assumed that the ordinary acoustic equations are applicable except as modified by the non-homogeneity and that the cross section is small enough so that transverse motions may be neglected. It is then found that the problem of determining the allowed vibrations in such a tube satisfying the boundary condition that the condensation $s=\delta\rho/\rho_0$ (where ρ_0 is the equilibrium density at any point and $\delta\rho$ the excess density) shall remain analytic, everywhere $<<1$ and vanish at infinity, is formally equivalent to the problem of solving a one-dimensional Schrödinger wave equation subject to the usual boundary condition. The appropriate density variation and the shape of the tube are shown to be related to the potential energy of the particle whose motion is described by the Schrödinger equation. As illustrations the free particle, the simple harmonic oscillator and the one dimensional hydrogen atom are investigated. It is believed that generalization to three dimensions will prove possible.

40. A general formulation of the uncertainty principle and its classical interpretation. H. P. ROBERTSON, *Princeton University.*—Denoting the mean value of a quantum mechanical variable α in a state ψ by α_0 and its uncertainty or standard deviation by $\Delta\alpha$, the uncertainty principle $\Delta\alpha \cdot \Delta\beta \geqq (h/4\pi)|\gamma_0|$, where $(h/2\pi i)\gamma$ is the commutator $\alpha\beta-\beta\alpha$ of α and β, is obtained for general systems, which may include spin. It is found to be a consequence of the more restrictive inequality $\Delta\alpha \cdot \Delta\beta \geqq \{[(\alpha\beta)_0-\alpha_0\beta_0][(\beta\alpha)_0-\beta_0\alpha_0]\}^{\frac{1}{2}}$. The former result is interpreted classically as meaning that we can only determine that two quantities $\alpha(p, q)$, $\beta(p, q)$ have values lying between $\alpha_0 \pm \Delta\alpha$, $\beta_0 \pm \Delta\beta$ provided the integral invariant $J=|\Sigma(i)\int p_i dq_i|$ taken over the area normal to these four hypersurfaces in phase space is at least of order h.

41. Thomson effect in zinc crystals. L. A. WARE, *University of Iowa.*—The Thomson coefficient, σ, is directly determined for a group of zinc crystal rods with orientations distributed fairly uniformly over the entire possible range of orientations. At 49.5°C, and at 125°C, the values of σ seem to obey the Voigt-Thomson symmetry relation, although not as good a check is obtained at the higher temperature due probably to increased experimental error. The principal values obtained are: at 49.5°C, $\sigma_\perp = 0.98\times10^{-6}$, $\sigma_\parallel = 0.38\times10^{-6}$; at 125°C, $\sigma_\perp = 2.09\times10^{-6}$, $\sigma_\parallel = 1.08\times10^{-6}$ Cal./coul./degree C. The increase of σ with increased temperature is greater than has been previously reported for polycrystalline zinc but is in approximate agreement with some earlier determinations by the writer. In addition, specific resistivity and temperature coefficient of resistivity are determined.

42. Thermal expansion of copper-nickel-tin alloy. PETER HIDNERT AND W. T. SWEENEY, *Bureau of Standards.*—In 1926 determinations were made at the Bureau of Standards on the inear thermal expansion of a copper-nickel-tin alloy known as Admiralty nickel or Adnic. It s claimed that this white nickel alloy resists corrosion and shows good strength at elevated temperatures. The sample, 1–3/10 inches in diameter, was extruded from 1–3/8 inches and finished hard with a 1/16 inch draught after a suitable anneal. The chemical analysis was as follows: Copper 69.57, nickel 28.70, tin 0.91 percent. Scovill Mfg. Co., Waterbury, Conn. prepared the sample and furnished information about the treatment and the chemical composition. The following coefficients of linear expansion were obtained:

Temperature Range	Average Coefficient of Expansion per Degree Centigrade
20 to 100°C	15.2×10^{-6}
100 to 200	15.5
200 to 300	18.0
20 to 200	15.4
20 to 300	16.3

Data on physical properties of this alloy are given in Mining and Metallurgy **8,** 474 (1927).

43. A new method for measuring the variation of specific heats of gases with pressure. E. J. WORKMAN, *University of Virginia.*—The method determines the ratio of c_p at a high pressure to c_p for the same gas at a pressure of one atmosphere taken as a standard. The continuous flow principle is used in such a way that the necessity for measuring rates of gas flow and heat input is avoided. A stream of gas at high pressure is brought to a temperature t_1 and passed through a heat interchanger acquiring there a temperature t_2, after which it is throttled to atmospheric pressure, brought to a temperature t_3 and returned to the heat interchanger, where its temperature again becomes t_2. If there is no heat leakage the ratio of c_p at high pressure to that at atmospheric pressure is equal to $(t_3-t_2)/(t_2-t_1)$. Measurements on commercial oxygen taken at a mean temperature of 26°C and pressures ranging from 15 to 100 atmospheres indicate, when corrected, a pressure coefficient in this ratio 0.0017 ±0.0001 per atm.

44. The effect of hydrogen ion concentration on the measurement of the mean particle size of emulsions. ISABEL C. WEEKS, *The Pennsylvania State College.* (*Introduced by Wheeler P. Davey.*)—W. P. Davey proposed (Science **64,** 252 (1926)) measuring the mean particle size of emulsions by a water-spreading method. The present work investigates the effect on such measurements of the pH(=1/log concentration of H^+) of the water used. Three emulsions were tested, stabilized with the sodium soaps of myristic, palmitic and stearic acids respectively. The pH was varied from 3.0 to 11.0 by means of buffer solutions. No effect was found traceable to the buffer materials used. At a pH less than 7.0 (i.e. the water is acid) the area of the water-spread emulsion for a given pressure increases with time without reaching an equilibrium value. At a pH greater than 7.0 (i.e. the water is alkaline) the area for a given pressure finally becomes constant with time, but the values are large and depend upon the pH. In every case the emulsion area was corrected for the area covered by pure buffer. At $pH=7.0$ (i.e. the water is neutral) the water-spread emulsion shows a constant area with time for a given pressure, and reaches equilibrium very quickly. Areas found at $pH=7.0$ are therefore taken as the true areas to be used in plotting pressure-area curves for particle-size calculations.

45. Molecular aggregation. A. M. TAYLOR. *Institute of Applied Optics, Rochester, N. Y.* (*Introduced by T. R. Wilkins.*)—A brief résumé of the lines of evidence by which molecular aggregation in pure liquids may be recognized; from the surface tension, from viscosity, from optical anisotropy, and from the Raman effect. The question of molecular size in the solid state can at present be answered only by x-ray analysis and by comparison of specific heat data with theory. A third method is suggested based on the Vant-Hoff equilibrium equation $d(\log k)/dt=Q/RT^2$. Q is here the differential heat of solution of the solid in a given solvent, while k is the equilibrium constant regulating the exchange between the molecules in the solid and the molecules in the solution; k may be expressed in terms of the change of solubility with temperature. For iodine the method gives I_2 as the molecular size in the solid state; this agrees with x-ray measurements which show that solid iodine has a molecular lattice of I_2. Lack of data prevents further application of the method at present.

51. Phenomena in oxide coated filaments. E. F. LOWRY, *Westinghouse E. & M. Co., East Pittsburgh.*—It has been suggested in a previous paper that the phenomena of oxide emission might be explained by assuming that the source of electron emission is a layer of metallic barium occluded on the surface of the core metal. The activity of such a filament is characteristic of this composite surface and the peculiar effects met with are due to the diffusion of the electrons through the pores of the oxide coating. In the present paper experiments are described which tend to support this view. Filaments made by vaporizing metallic barium on clean Konel ribbon give emissions of the same magnitude as those coated with oxide in the usual way but approach saturation rapidly while oxide filaments approach saturation very gradually if at all. The "three halves power" law is obeyed exactly by both types. "Bariated" Konel filaments show very little if any "fading" of emission with time, while considerable fading is experienced with oxide filaments, particularly in a certain range of temperatures and with heavy coatings. No activation of these filaments is necessary other than thermal decomposition of the alkaline earth carbonates in vacuum.

52. Density distribution of electron gas in equilibrium with a hot body. A. T. WATERMAN, *Yale University.*—The variation of potential and of electron concentration with distance from a plane emitting surface is investigated, using Poisson's equation and the equilibrium relation between electron concentration and potential in the form $A=A_0e^{-V\epsilon/kT}$, where A and A_0 are the Fermi A's outside and inside the hot surface, respectively, and V is the corresponding potential difference. Solutions are found for the equilibrium condition in the absence of applied field and for negative fields, and assuming the electron gas within the body to be degenerate or classical. Results indicate: (1) that on the average an electron is closer to its neighbors than to the surface, except when very close to the latter, and therefore that the image force explanation of the work function is here not applicable; (2) that space charge is quite competent to give the magnitude of the work function; (3) that if the electron concentration within the body

is that of the atoms, the external gas remains degenerate to approximately 10^{-7} cm from the surface; (4) that an applied negative field of the magnitude required for cold field currents materially alters the electron concentration down into the degenerate region. The current obtainable under retarding fields is discussed with a view to estimating the feasibility of experimental proof of the relations established and of the electron concentration within conductors.

53. A space charge interpretation of thermionic work function. RUSSELL S. BARTLETT, *Yale University.*—We try to account for the thermionic work function by the space charge field of electrons streaming out from the surface and turning back in this same field. To account for the increase in thermionic currents in strong electric fields it is necessary that the work function field extend so far out that an escaping electron is much nearer to its neighbors than to the surface. If we extend Fry's space charge analysis, with classical velocity distribution, right down to the surface of the metal, assuming an electron concentration about midway in the range of prediction, we find something resembling saturation currents, a suitable value for the work function, and an increase of current with strong fields agreeing better with experiment (Proc. Roy. Soc. **A121,** 456 (1928)) than does Schottky's expression depending on image force alone. A first order correction for Fermi-Dirac distribution brings improvement, though the variation of work function with temperature is too great. But the strict application of the Fermi-Dirac statistics for a degenerate gas, with its large zero point energy, should remove that difficulty, and should provide for an explanation of field currents, since the large fields necessary should penetrate into the region of degeneracy.

54. Effective photoelectric work function reduced by weak accelerating fields. W. B. NOTTINGHAM, *Bartol Research Foundation.*—Photoelectric experiments on thin alkali metal films reported (Phys. Rev. **33,** 633 and 1081 (1929)) seemed to indicate a nonlinear relation between current and light intensity and a departure from Einstein's photoelectric equation. A study of amplifier-galvanometer systems for measuring small currents (Journal of Franklin Institute, March 1930), showed that the nonlinearity was in the current measuring system. A thin alkali metal film on nickle or platinum changes the work-function (ϕ) of the surface by a small amount, and greatly alters the space distribution of the electric field against which the electron must work in order to escape. This redistribution makes it possible to reduce the *effective* work-function (ϕ_e) of the surface by applying a small accelerating field. The photoelectric long wave-length limit is a direct measure of ϕ_e. With a retarding field, ϕ_e is greater than ϕ and the Einstein equation gives the relation between ϕ_e and the potential. At zero field, $\phi_e = \phi$ while with an accelerating field, ϕ_e is less than ϕ. For example, ϕ_e has been observed to be reduced by 1.95 volts by the application of an accelerating potential of 4 volts between the electrodes. A further increase in accelerating potential to 750 volts gave a further decrease in ϕ_e of only 0.32 volt.

55. Photoelectric properties of extremely thin films of alkali metals. HERBERT E. IVES AND H. B. BRIGGS, *Bell Telephone Laboratories.*—Films of alkali metal much thinner than those previously studied (Astrophys. J. **60,** 209 (1924)) have been investigated by using an electrometer of approximately 100 times the sensitiveness of the galvanometer used before. Attention has been directed to the variation of emission with the angle of incidence and plane of polarization of the exciting light. In agreement with the earlier work, the ratio of emissions for obliquely incident light polarized with the electric vector in and perpendicular to the plane of incidence decreases as the film is reduced in thickness. The new measurements show further that this ratio continues to decrease with film thickness to the value unity, where no variation of emission with angle occurs, and that with further decreases in film thickness, the relationship *reverses,* ("normal" greater than "selective") and the emission increases with the angle of incidence of the light. It is suggested that when the alkali metal particles become sparsely distributed their absorption of light corresponds to that of a matt surface (Lambert's law). When the particles are still more widely separated, deviation from Lambert's law occurs and the exciting light is in part that reflected from the underlying platinum surface, stronger for light polarized with the electric vector parallel to the surface.

56. Validity of Einstein's photoelectric equation for red sensitive sodium compounds. A. R. OLFIN, *Bell Telephone Laboratories, Inc.*—Using a photoelectric cell specially designed so that the cathode could be sensitized in a side compartment and then slipped into position within a soot-coated nickel anode, stopping potentials were obtained for electrons liberated by highly resolved light of wave-lengths ranging from 3500A to 8000A. The cathode consisted of a nickel plate heavily coated with sodium and specially treated with sulphur and air [abstract 57 Bull. Am. Phys. Soc. 4, 2 (1929)]. The anode of such a cell is not sensitive to light, so the voltage at which the emission from the cathode just becomes zero is a measure of the true stopping potential. Plotting the voltages so obtained versus the exciting light frequencies a perfectly straight line is obtained. From the slope of this line, a value of Planek's constant *h equal to* 6.541×10^{-27}, significant to three figures, is obtained. It is possible with one cell to obtain stopping potentials for electrons released from sodium before and after treating it with sulphur and air. In such cases the voltage at which the photoelectric emission ceases is the same, but after treatment the current saturates at a higher voltage, exhibiting a change in the contact difference of potential of 0.8 volt.

57. Photoelectric cell thermoregulator. F. G. BRICKWEDDE AND R. B. SCOTT, *Bureau of Standards, Washington, D. C.*—Recently a photoelectric cell was used with a thermocouple as the thermosensitive element to make a new kind of thermo-regulator. There are many laboratory problems requiring automatic regulation to which the photoelectric cell can be applied. Photoelectric cell regulators possess great sensitivity, small lag and a wide range of temperatures over which they can be used and be quickly and conveniently adjusted for operation at any desired temperature. The parts of the thermo-regulator are analyzed and it is shown how they can be modified to adapt this regulator to special problems. Improvements are described and causes of trouble pointed out. A photoelectric regulator has been made which will automatically maintain any temperature from 0° to liquid air temperatures constant to 0.001°. It is operated on a 240 volt D.C. power, without batteries, using only one slide wire rheostat with four sliding contacts to furnish all the sources of potential for the photoelectric cell and its amplifier thus making the regulator less expensive and obviating all the inconveniences of run down batteries.

58. Apparatus for maintaining constant low temperatures. R. B. SCOTT AND F. G. BRICKWEDDE, *Bureau of Standards, Washington, D. C.*—A cryostat of improved design for use in the temperature range from 0°C to liquid air temperatures has been constructed. The cryostat bath is contained in a double-walled cylindrical glass vessel surrounded by liquid air, and the amount of refrigeration controlled by varying the air pressure between the walls. Constant temperature is automatically maintained by the use of a photoelectric cell thermoregulator operating a heating coil on the stirrer tube. Adequate circulation of the liquid, careful heat insulation, and symmetrical distribution of all the parts assure great uniformity of temperature. The temperature is easily adjusted to the desired value and can be maintained constant to 0.001°C. Nonflammable liquids are used for the bath between 0°C and −150°C.

59. Raman spectra excited by the helium hot-cathode arc and a new type of tube for small volumes of liquid. R. W. WOOD, *Johns Hopkins University.*—A hot-cathode helium arc of great brilliancy, carrying three amperes, kindly supplied by the research laboratory of the General Electric Company of Schenectady, has been very successfully used in combination with a filter of nickel oxide glass for the excitation of Raman spectra. Exposures of less than three hours are required as against fifteen hours with the spiral tube which I described last year. A new type of tube for the investigation of volumes of only eight or ten cubic centimeters of liquid has been developed, adapted to the investigation of liquids of low boiling point or solids which liquify below 100°C.

60. The calculation of the specific heats of solid organic compounds from Raman spectra. DONALD H. ANDREWS AND JOHN C. SOUTHARD, *The Johns Hopkins University.*—It seems to be possible to identify the lines in the Raman spectra of a number of organic molecules with

definite modes of vibration in the molecule (see abstract Number 25). This permits the assigning of the correct number of degrees of freedom to each frequency and it is found that the sum of the degrees of freedom so assigned has a value consistent with the number of atoms in the molecule. If we then consider that the various modes of vibration in the molecule act as independent Einstein oscillators, it is possible to employ the frequencies from the Raman spectra and calculate the specific heat of the molecule for any temperature. This has been done for methyl alcohol, ethyl alcohol, benzene, toluene, chlor benzene and brom benzene over the temperature range of 15° to 260°K. The average deviation between the results so calculated and the experimental values is about five percent.

61. Mosaic crystals of elements. R. H. CANFIELD, *Naval Research Laboratory, Anacostia, D. C.*—Assuming that the atoms of a crystal of an element are all exactly alike and exert mutual central forces, and that the force between any two atoms vanishes for only one value of the distance, it is found that the conditions of stability of equilibrium of the crystal against an infinitesimal generalized strain require that certain series of terms in the second derivatives of the energy function shall be greater than zero. If this is granted, it is shown that any translation of a part of the perfect crystal relative to the remainder causes the potential energy of the lattice to increase. Hence all such imperfections are to be regarded as unstable.

62. Selective maxima in the spectral response curves of light-sensitive compounds as a function of valence. A. R. OLPIN, *Bell Telephone Laboratories, Inc.*—Lindemann proposed a formula for computing the frequency of light under excitation by which a substance should yield electrons most readily. This formula, $\nu = (1/2\pi)\left[(ne^2)/(mr^3)\right]^{1/2}$, gives the frequency of an electron revolving in an orbit of radius r about a stationary charge ne [m = mass of electron]. The n term is determined by the valence of the substance, a choice of unity for the monovalent alkali metals corresponding to an electron revolving around a singly charged ion. With the normal valence of the alkali metals, Lindemann computed selective frequencies which have been checked by many observers. Under certain conditions, the alkali metals manifest different valences, such, for instance, as those exhibited in the oxide series Na_2O_2, Na_2O, Na_3O, Na_4O. These compounds are light sensitive and can be prepared in photoelectric cells. Spectral response curves for such cells exhibit all the selective maxima called for by the Lindemann formula when the value of n is chosen to agree with the valence of the metal. Data are presented showing this condition to be general for the other alkali metals, a maximum response to red or infra-red light being dependent upon the formation of a subvalent compound, as a suboxide.

63. The scattering of atomic hydrogen by gases: mercury, argon, oxygen and iodine. E. G. LUNN AND F. R. BICHOWSKY, *Naval Research Laboratory.*—A beam of hydrogen atoms defined by two small holes passes through a gas-filled space and impinges on a plate coated with molybdenum trioxide. The loss in intensity of the beam due to collision of the hydrogen atoms with molecules of the various gases depends on the sum of the radii of the hydrogen atom and the gas molecules. The collision diameter of the hydrogen atom can then be calculated directly and simply by using the known collision diameters of the several gases. While the collision diameter of hydrogen determined by comparison with mercury is about eight Angströms, that calculated from preliminary results on the scattering in argon and oxygen is about two Angströms. Similar measurements in iodine, made uncertain by a fading of the reduced molybdenum oxide due to oxidation by the atomic iodine formed, indicate a collision diameter of over twenty Ångströms. The collision diameter is thus a property of the degree of interaction between the colliding particles. This is in accordance with the Heitler and London picture of chemical reaction.

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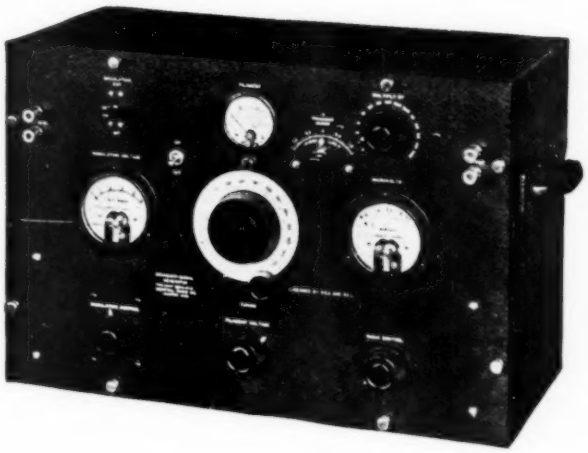

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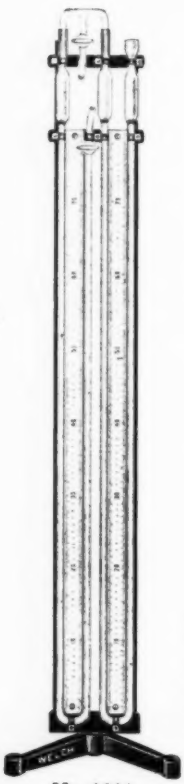

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